A SPECTROSCOPIC STUDY OF THE SELF ASSOCIATION OF SOME ALKYL PHENOLS

by

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INTRODUCTION

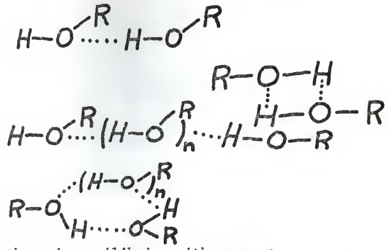
The study of the hydrogen bond has been in the past and probably will be in the near future almost entirely an experimental effort since present theory, even at best, can give only qualitative information about the equilibrium processes. Since the association processes taking place considerably affect most physical properties many classical physical techniques have been used to study these processes. Some examples are dielectric measurements, gas imperfections, cryoscopic and solubility investigations (1). The major difficulty with most classical physical measurements is that they give information associated with bulk or macroscopic changes in a material and not information associated directly with the molecular associations. Spectroscopic studies showed great promise for quantitative study of these equilibrium processes since the intensity variations of bands with temperature and concentration could be correlated with the equilibrium species of the association processes. In general the equilibrium process may be thought of as an acid (electron deficient hydrogen atom in a molecule) associated with a base (electron abundent portion of a molecule) or $A + :B \rightleftharpoons A\cdots :B$. Self association as used here is defined as intermolecular association as opposed to intra-molecular association. The association of alcohols and phenols takes place between the hydroxyl hydrogen of one alcohol molecule and the oxygen of another alcohol molecule. Consequently, the self association of alcohols can be realized in four ways:

i) linear dimer

ii) cyclic dimer

iii) linear polymer

iv) cyclic polymer



or any combination of these in equilibrium with monomer.

In the past it was generally believed that, if the concentrations were kept sufficiently low the alcohol would be present in monomer-dimer equilibrium making the quantitative study easy since each species could be characterized from infrared spectra. The free OH stretching mode of alcohols and phenols occurs above 3600 cm^{-1}. The band appearing in the infrared spectrum near 3500 cm^{-1} at low alcohol or phenol concentration, being temperature dependent at constant concentration (intensity increases as temperature decreases) was assigned to the dimer. Fletcher and Heller (2) have recently questioned the assignment of the 3500 cm^{-1} band to dimers in alcohol systems. They cautioned against the <u>a priori</u> selection of a certain self association model and fitting the mathamatical treatment to the selected equilibrium. The results of their work which was done on 1-octanol and 1-butanol in n-decane could be explained satisfactorily by monomer in equilibrium with linear and cyclic tetramers without the presence of dimers.

The assignment of the 3500 cm^{-1} band to dimer for the three alcohols methanol, <u>t</u>-butanol and di-<u>t</u>-butyl carbinol in carbon tetrachloride has been confirmed by Hammaker, <u>et al</u>. (3). The assignment of this band to dimer for methanol in carbon tetrachloride has also been confirmed by Fletcher and Heller (4).

Prior to the appearance of the work of Fletcher and Heller (2) an investigation was carried out on 2-alkyl and 2,6-dialkylphenols using nuclear magnetic resonance spectroscopy employing a technique of date analysis which required the assumption of only monomer-dimer association (5). The investigators in this study had taken the appearance of the bonded absorption band near 3500 cm^{-1}, whose shape was concentration independent over the concentration range used in the nuclear magnetic resonance experiments, as satisfactory evidence that only dimerization was occuring in these substituted phenol carbon tetrachloride systems (5).

At the onset of the present study it seemed mandatory to attempt to determine unequivocally the stoichiometry of association and to either confirm or deny the presence of dimers for the alkyl phenols in carbon tetrachloride solutions. The compounds selected for this study was 2-*iso*propylphenol, 2-*tert*-butylphenol, 2,6-di*iso*propylphenol and 2-methyl-6-*tert*-butylphenol. These were selected to give a variation in the sterical hindrance to hydrogen bond formation. The method used was that of Hammaker *et al*. (3), which employs the ratio of the absorbance per cm. path length of the infrared band at 3500 cm^{-1} (A_f) to the absorbance per cm. path length of the first OH stretching overtone near 7100 cm^{-1} (A_o) raised to the $\underline{n}^{th}$ power. The near infrared band near 7100 cm^{-1} has been shown to be a measure of the uncomplexed or free OH concentration in alcohol systems (2,5). If A_f is taken as a measure of the complex concentration and A_o is taken as a measure of the monomer concentration, then $A_f/A_o^{\underline{n}}$ is proportional to the equilibrium constant for a monomer $\rightleftharpoons$ *n*-mer equilibrium.

The $\underline{n}$ giving the most constant value of this ratio over a range of concentrations at constant temperature is selected as the correct number of molecules combining to form the complex. Alternatively, if $A_f/A_o^{\underline{n}}$ is a constant over a concentration range at constant temperature a plot of Ln A_f vs. Ln A_o should take the form of Ln A_f = $\underline{n}$Ln A_o + Ln constant where $\underline{n}$, the slope, is the number of molecules in the complex.

An investigation of the change in the absorption coefficient with temperature in concentration ranges where Beer's Law is obeyed for the near infrared absorption spectra (ranges where no perceivable association is taking place) was also desired. Prior to the present study, Swenson (6) had reported a decrease in the absorption coefficient of the water, methanol and ethanol free OH fundamental with increasing temperature in carbon tetrachloride. His explanation was that as the temperature increased the vapor volume above the solution became enriched in the volatile solute, thus decreasing the concentration of the solute and causing the absorbance to decrease. The phenols used in this study are not as volatile so this affect should not be as great. For standard cells Hammaker (7) has shown that this explanation may not be adaquate, even for the volatile solutes in Swenson's study, since the vapor volume is usually very small and does not contain enough solute to decrease the concentration to the extent necessary to show the changes reported (6).

The method of A. Ens and F. E. Murray (8) can also be used to determine the number of molecules combining to form the complex. This method is analogous to the Ln A_f vs. Ln A_o plots described above in that Ln $(c-c_1)$ is plotted against Ln c_1, where c is the total concentration and c_1 is the monomer concentration. Here it is necessary to know the monomer absorption coefficient, a_m, in order to calculate $c_1 = A_o/a_m$ from measured A_o values. It is seen that $(c-c_1)$ is proportional to the concentration of the complex. A possible source of error in this type of calculation is that often in sterically hindered alcohol systems the value of the monomer concentration is very nearly equal to the total concentration. The difference between total and monomer concentration especially for the lower concentrations of alcohols used in the study is small, which gives rise to large subtraction errors. Another possible source of error in this calculation may result from the free OH end group of a linear complex (see structures i and iii on page 2) contributing to the free OH band absorbance and making the observed value larger than it would be if only free OH from alcohol monomers contributed to this band. Therefore, the calculated concentration of alcohol monomers, $c_1 = A_o/a_m$, would be larger than it should be and the difference between total concentration and the calculated monomer alcohol concentration will be too small thus giving a systematic error to the number of molecules in the complex determined from the slope of the $\text{Ln}(c-c_1)$ vs. Ln c_1 plot. The former error can be alleviated by using high enough concentration so that appreciable association will take place making a significant difference between the total concentration and the monomer concentration. However, then if the complex has a free end group the monomer concentration determined from the free OH band may be in error due to the large concentration of complex.

If one knows the stoichiometry of the association process then the end group contribution can be determined by using the technique of Masschelein (9). This method utilizes a plot of Ln $(c-\alpha_x c)$ vs. Ln $(\alpha_x c)$ where α_x is equal to the ratio of the observed absorption coefficient of the 7100 cm^{-1} band to the monomer absorption coefficient of the 7100 cm^{-1} multiplied by x where x is the fraction of the free OH band contributed by monomer. This plot will give decreasing slopes as x decreases. The value of x which gives the slope of the a priori selected or experimently determined number of molecules combined to form the complex is selected as the fraction of the 7100 cm^{-1} band intensity contributed by monomer.

If A_f/A_o^n is constant over a concentration range at a constant temperature, if the extent of association is low enough so that A_o has very little or no end group contribution, and if A_f is due to complexes of a single stoichiometry A_f/A_o^n is proportional to the equilibrium constant. The proportionality constant is a function of the absorption coefficients for both the fundamental and the overtone bands. If neither of the absorption coefficients are functions of temperature, a plot of Ln (A_f/A_o^n) vs. 1/T gives a correct enthalpy of complex formation. However, since it is believed that the absorption coefficients change with temperature the Ln (A_f/A_o^n) term must be corrected to give the correct temperature dependence of Ln K.

The intercepts from the Ln A_f vs. Ln A_o plots described above are also proportional to the equilibrium constant where the proportionality constant is again a function of the absorption coefficients. The derviation of the results is in Appendix A.

In this study the $\text{Ln}(A_f/A_o^2)$ values were corrected for changes in absorption coefficients to give an equilibrium constant. It is seen in Appendix A that if the complex is a dimer, the concentration of complex and monomer can be represented by A_f/a_f and A_o/a_m, respectively, and

$\text{Ln } K = [\text{Ln}(A_f/A_o^2) + \text{Ln } (a_m^2/a_f)]$ where a_m and a_f are absorption coefficients for the monomer at 7100 cm^{-1} and the species causing the 3500 cm^{-1} band, respectively. From this equilibrium constant and the enthalpy determined from plots of Ln K vs. 1/T, the thermodynamics of these association processes was investigated.

EXPERIMENTAL

The experimental work consisted of preparing solutions and running their spectra at different temperatures in the fundamental and first overtone regions of the OH stretching vibration. From the fundamental OH stretching vibration the absorbance of the band for the bonded OH complex was obtained and from the first overtone the absorbance of the band for the free OH was obtained.

Materials

The substituted phenols (2-isopropyl, 2-tert-butyl, 2,6-diisopropyl and 2-methyl-6-tert-butylphenol) were obtained from Aldrich Chemical Company Inc. and were purified by vacuum distillation through a 30 cm. Vigreaux column collecting the second constant boiling portion. The pressure was held constant using a manostat for each between 16 and 22 torr where the pure phenols distilled over in the 100 to 120 °C range. The purified phenols were then stored in a desiccator, with P_2O_5 as the dessicant, in screw cap bottles covered with aluminum foil since it was found that light caused the clear liquid to become yellow then dark brown over long periods of time. The carbon tetrachloride was spectranalyzed grade obtained from Fisher Scientific Co.. It was dried by placing a filled beaker covered with a watch glass in a desiccator with P_2O_5 as the desiccant for at least twenty-four hours.

Solutions

All solutions were prepared in a custom built dry box which had been purged for approximately five minutes with oil pumped nitrogen, which had been passed through a drying train filled with Linde type 13X molecular sieve prior to entering the dry box. After purging of the dry box was completed, the atmosphere of the dry box was circulated for thirty minutes before the solutions were prepared. The nitrogen in the dry box was circulated with an Air Control Co. Inc. Hydrovoid System consisting of a circulating pump (Dis-pump model EF-EFC-EFA) and an anodized aluminum train containing Linde type 13X molecular sieve.

The solutions were prepared by weighing both of the components in the dry box. The weighings were made on a Mettler H6 Digital Analytical Balance. The cells used for both spectral regions were Cary cylindrical type cells with near infrared quartz windows. The cells were filled in the dry box for the spectra taken in the infrared region and in a plastic glove bag purged with oil pumped nitrogen for the spectra taken in the near infrared region.

Spectrophotometers

The instruments used in this study were Perkin-Elmer 337 and Cary model 14R recording spectrophotometers. The Perkin-Elmer 337 double beam spectrophotometer was used to study effects of temperature and concentration on the fundamental OH stretching vibrational spectra. This is a grating instrument recording linearly in cm^{-1} giving a continuous spectrum of the infrared transmittance of a sample as a function of the frequency. The resolution of this instrument is $\sim 7\ cm^{-1}$ near $3500\ cm^{-1}$. The instrument was turned on and allowed to warm up for about 15 minutes. Then with the slit width normal, and the recorder on, the one hundred and zero percent transmittance was set and checked. The high frequency range (4000 to $1200\ cm^{-1}$) and fast scan were employed to obtain the spectra of the fundamental OH stretching vibration.

The Cary 14R double beam spectrophotometer, recording linearly in wavelength, was used to obtain the first overtone spectra of the OH stretching vibration as a function of temperature and concentration. The spectra in both regions were run at the same temperature using solutions of very nearly the same concentration, if not actually the same solution. The source used for the Cary 14R near infrared region was a tungsten lamp. The instrument was operated in the mode where monochromic light was incident on the cells. A scan speed of 5 Angstroms per second was used in recording spectra on chart paper which had a speed of 1 inch per minute.

Temperature Control

The temperature for the fundamental spectra was controlled through the use of a Barnes Engineering Company variable temperature chamber (VTC-104). The chamber is a cubical box designed to mount directly in the sample beam of all Perkin-Elmer and Beckman spectrophotometers. It is constructed of rigid polyurethane foam in an outer aluminum casing. It was suppled with KBr thermopane windows; however, at low temperatures water condensed between the original windows supplied by the manufacturer causing considerable absorption in the OH stretching region. These windows had been cracked and apparently water vapor had leaked in between the windows. New thermopane windows were made by epoxy glueing (Torr Seal low vapor pressure resin obtained from Varian Associates) two polished calcium fluoride windows to each side of a plastic washer leaving a "dead" air space between the windows; this was done for each end of the chamber. The unpolished calcium fluoride windows obtained from Optovac Inc. were polished using 3 micron polising grit, on a

Politex Pad, (Geoscience Instruments Co.). The solvent was dilute HCl. They were polished until each single window would transmit 90 percent of the incident radiation _versus_ air at 4000 cm^{-1} as determined by the Perkin-Elmer 337 spectrophotometer. It was also necessary to design and build a cell holder inside of the chamber to accomodate the Cary cylinderical cells. (This was accomplished by attaching a curved piece of metal about 1 inch long, to support the cells in the beam, to a second piece of metal which fits the standard mount. The metal portions of the holder which would come in contact with the cells were covered with felt.)

The temperature was regulated inside of the chamber by supplying direct current to "heat pumps" that utilize the Peltier effect, that is when a direct current is applied to the junction of two dissimilar metals, such as a thermocouple, one junction will become cooled and the other heated. In this chamber a bank of bismuth-telluride junctions are mounted in direct contact with the walls of the inner chamber. A circulating stream of tap water is used to transport the heat from the chamber.

The chamber was equipped with a copper constantan thermocouple to measure the temperature inside of the chamber. Since the Perkin-Elmer 337 is constructed so that non-monochromatic light is passed through the sample the temperature of the sample was found to be higher than that of the inner chamber. It was, therefore, necessary to determine the cell temperature in relation to that of the inner chamber. This was accomplished by placing a cell filled with carbon tetrachloride in the beam and simultaneously measuring the temperature of the inner chamber with the thermocouple and the cell temperature with a Yellow Springs Instrument Co. thermistor at approximately 5 minute intervals for 30 minutes. It was found that after about 20 minutes time the cell temperature became fairly constant. The proper setting for the desired temperature of the input voltage and the coolant flow rate of the water was determined and used in the experiments. By this method the cell temperature could be monitored to $\pm$ 1 °C. These values are shown in Table I.

At 0 and 15°C water condensation on the windows was alleviated by passing oil pumped nitrogen around the outside of the chamber following passage through a Linde 13X molecular sieve column. The entire sample and reference area of the Perkin-Elmer 337 was covered with a piece of polyethylene taped to the instrument housing so that the nitrogen would flush the instrument.

The temperatures for the near infrared spectra were controlled in an entirely different manner. The Cary 14R cell holders are constructed so that either a cooling or heating fluid can be circulated through them. For temperatures higher than room temperature, a Haake Circulator model F was employed. It has a built-in heater that is thermostated so it can be set at a desired circulator fluid temperature. The circulator fluid used in this circulator was water. For temperatures below room temperature a second circulator containing 45% ethanol for the circulator fluid was used. The circulator fluid was cooled by equipment designed and built by P. E. Rider (10) which employs the use of an auxiliary coil submerged in a dry ice isopropanol mixture in a large Dewar flask. The ethanol was circulated until the desired temperature was attained in the cell compartment. The temperature was held constant for about ten minutes before the spectra were run so the contents of the cell had time to come to thermal equilibrium. The temperature in the cell compartment was measured with a Yellow Springs Instrument Co. thermistor

Table I: Temperature Control Settings for the Fundamental Spectra

Power Switch	Dial Setting	Input Voltage	Inner chamber Temperature	Cell Content Temperature	Flow Rate of Coolant
Heat or cool	Variable transformer	Volts 0-150V AC	°C	°C	ml/min.
cool	65	73	-14.0	0.0	600
cool	25	28	1.0	15.0	600
heat	5	6	14.3	26.0	600
heat	10	12	23.5	34.7	600
heat	20	25	36.8	45.2	600

and could be held to $\pm$ 1 °C at 0 and 15°C and $\pm$ 0.1 °C at the other temperatures while the spectra were being recorded. Here again the water condensation problem was alleviated by purging the cell compartment with dryed (by passage through a molecular sieve column), oil pumped nitrogen.

Density Measurements

Due to the inaccuracy of filling the volumetric flasks in the dry box only the weights of each of the components of the solutions were accurately obtainable. The molarity which was needed to study the effects of temperature on the absorption coefficient, was therefore not directly calculable since the volume of the solution was not known. Consequently, the density was needed for each solution at each temperature to calculate the volume occupied by the solution at that temperature. The molarity was then calculated at each temperature.

The density of each solution was measured at room temperature by using a ten milliter volumetric flask and weighing the contents by difference on an analytical balance. The results are shown in Table II. The densities for the solutions at all other temperatures were obtained by applying a density unit change per degree of 1.75 x 10^{-3} for this type of solution. This value was determined by averaging the change in density per degree for several solutions. Knowing the density at each temperature the molar concentration at each temperature was obtained by taking the molar concentration at 25°C times the ratio of the density at the new temperature to the density at 25°C. Typical corrections for changes in molarity with temperature would result by multiplying the

Table II: Density of Alkyl Phenol-Carbon tetrachloride solutions at 25° C

conc. moles/liter	density grams/ml.	conc. moles/liter	density grams/ml.
2-*tert*-butylphenol		2-*iso*propylphenol	
0.0412	1.5737	0.0477	1.5702
0.0460	1.5685	0.0919	1.5616
0.0719	1.5541	0.0994	1.5561
0.1438	1.5435	0.1451	1.5430
0.2190	1.5256	0.2471	1.5380
0.3613	1.4876	0.2920	1.5200
0.4791	1.4762	0.3904	1.5042
2,6-di*iso*propylphenol		2-methyl-6-*tert*-butylphenol	
0.0556	1.5727	0.0707	1.5715
0.1158	1.5703	0.1458	1.5651
0.2423	1.5538	0.1830	1.5592
0.4309	1.5266	0.3906	1.5401
0.5307	1.5199	0.4928	1.5259
0.6523	1.5010	0.9667	1.4800
0.8430	1.4687	1.2841	1.4575
1.2758	1.4347	1.4570	1.4276
1.4688	1.4064	1.4771	1.4146

molar concentration at 25°C by the following density ratios:

°C	
0	1.0278
15	1.0111
25	1.0000
35	0.9889
45	0.9777

Recording Spectra

Representative spectra for each of the compounds are shown in Figures 1 through 4. Figures 1 and 2 are the fundamental spectra and Figures 3 and 4 are the overtone spectra of the corresponding compound. The fundamental spectra were taken in a 0.1 mm cell for the 2,6-dialkyl phenols and in 1.0 mm and 1.0 cm cells for the 2-alkyl phenols. The overtone spectra were taken in a 1.0 cm cell for the 2-alkyl phenols and in 1.0 mm and 1.0 cm cells for the 2,6-dialkyl phenols.

The fundamental spectra were taken using the Perkin-Elmer 337 with the sample cell run vs. air. The baseline was found to be temperature independent when run on CCl_4 vs. air. Consequently, the spectrum of CCl_4 at 25°C in the Cary quartz cell vs. air was drawn on each sample spectrum vs. air as the baseline. The absorbances for the OH stretching band near 3500 cm^{-1} are shown in Table III.

The overtone spectra were taken using the Cary 14R as a double beam spectrophotometer. However the peak height absorbances recorded by the Cary 14R had to be corrected since the optics of the Cary 14R using these cells with CCl_4 in both beams have some absorbance in this region. It was found that 0.015 absorbance units should be subtracted from the recorded peak maximum to give the correct overtone absorbances which are shown in Table IV.

The absorbances per cm cell length for the fundamental and the overtone of the OH stretching vibration are shown in Tables III and IV, respectively. For 2-tert-butylphenol and 2-isopropylphenol two bands occur in the fundamental below the free or uncomplexed band (band near 3600 cm^{-1}) and both are believed to be due to complex. These are designated as band I and II where band I is nearer the free OH band. Tables III and IV contain the concentration at 25°C with the absorbances at all experimental temperatures. These tables, therefore, contain all of the primary experimental data.

The intensity of the fundamental bands due to complex were used as a measure of complex concentration. The intensity of the first OH stretching overtone band was used as a measure of the free OH concentration.

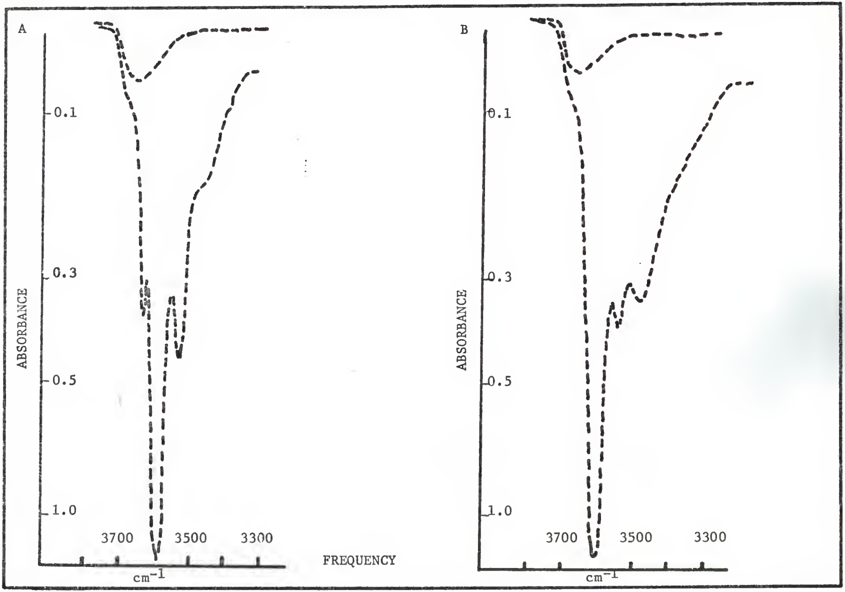


Figure 1 Fundamental Spectra A: 2-<u>tert</u>-butylphenol (0.2231 M CCl_4 Solution: 1 mm cell)

B: 2-<u>iso</u>propylphenol (0.2416 M CCl_4 Solution: 1 mm cell)

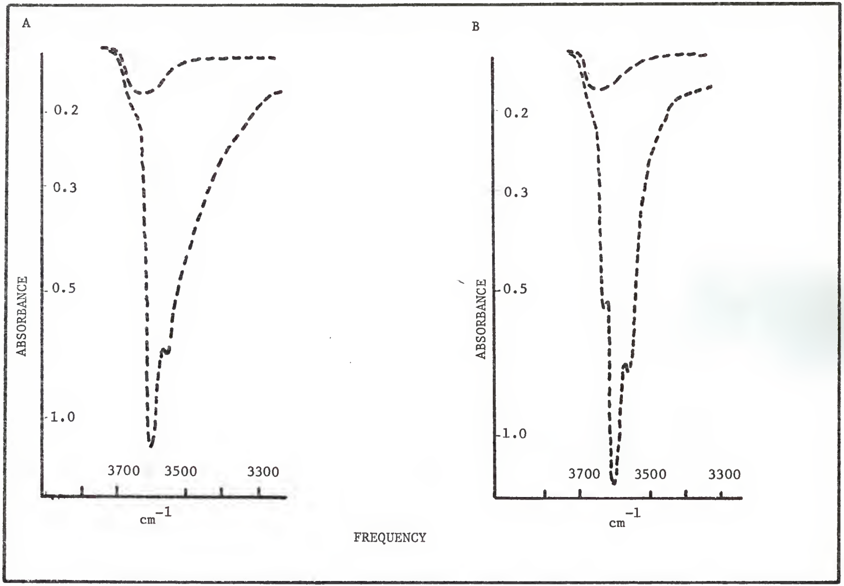


Figure 2 Fundamental Spectra

A: 2,6-di*iso*propylphenol(1.4688 M CCl_4 Solution: 0.1 mm cell)

B: 2-methyl-6-*tert*-butylphenol(1.4771 M CCl_4 Solution: 0.1 mm cell)

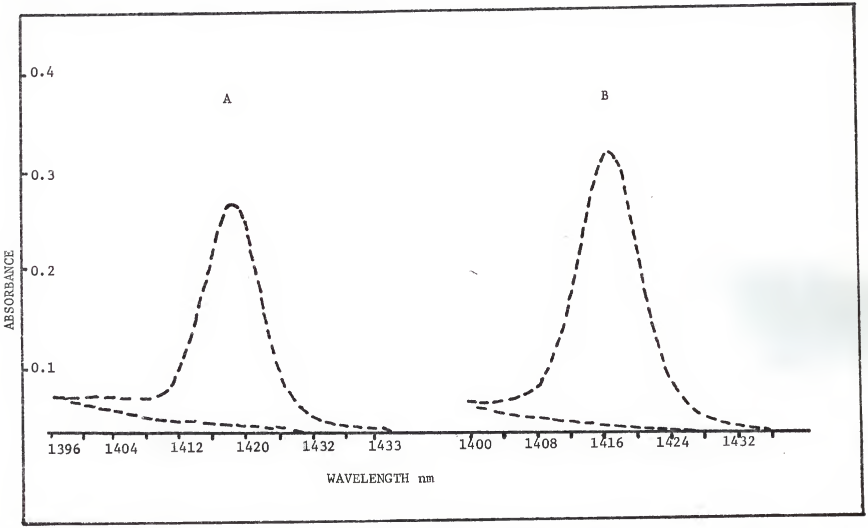


Figure 3 Overtone Spectra A: 2-tert-butylphenol (0.0719 M CCl_4 solution: 1.0 cm cell)

B: 2-isopropylphenol (0.0994 M CCl_4 solution: 1.0 cm cell)

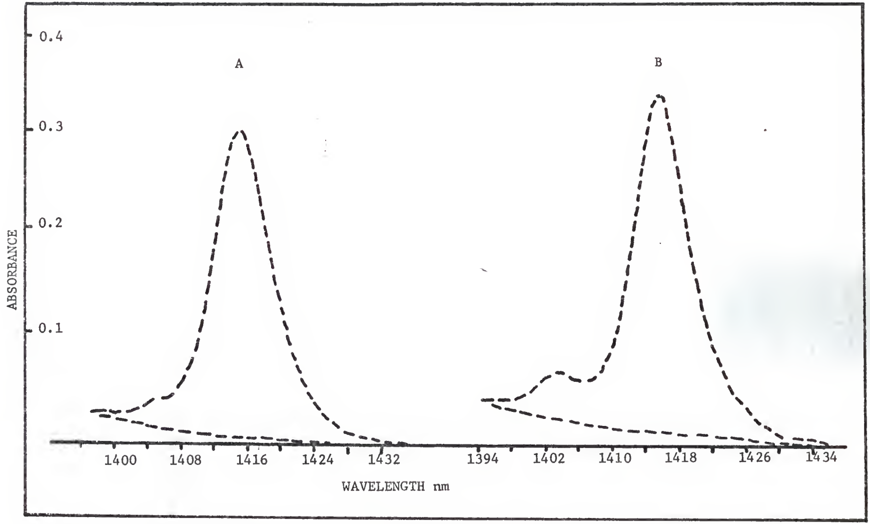


Figure 4 Overtone Spectra A: 2,6-diisopropylphenol (0.1158 M CCl_4 Solution: 1.0 cm cell)

B: 2-methyl-6-tert-butylphenol (0.1458 M CCl_4 solution: 1.0 cm cell)

Table III: Absorbance Per cm Cell Length for Fundamental Transition

conc. at 25° moles/liter	0°	15°	25°	35°	45°
	2,6-Di*iso*propylphenol				
0.6523	13.7	12.7	10.7	8.6	8.3
0.8430	21.1	21.5	21.6	21.4	21.2
1.2758	25.2	26.1	26.1	26.7	26.5
1.4688	27.8	28.8	29.0	29.6	29.6
	2-methyl-6-*tert*-butylphenol				
0.9667	27.6	25.5	23.0	22.3	22.8
1.2841	43.3	38.7	37.3	34.6	34.6
1.4570	52.8	47.7	45.5	42.5	41.5
1.4771	53.4	49.0	46.5	44.1	42.5
	2-*iso*propylphenol		band I		
0.0808	0.645	0.544	0.483	0.447	.....
0.1330	.....	1.258	0.985	.....	0.970
0.2416	4.87	4.23	3.67	3.50	3.07
0.2920	7.15	6.27	5.44	5.13	4.65
0.3820	10.00	8.70	7.87	7.48	6.84
			band II		
0.0808	0.754	0.556	0.413	0.362	.....
0.1330	.....	1.331	1.062	0.897	0.816
0.2416	5.90	4.56	3.10	2.99	2.53
0.2920	8.48	6.72	4.90	4.44	3.78
0.3820	12.01	9.25	7.57	6.61	5.69
	2-*tert*-butylphenol		band I		
0.0675	0.465	0.326	0.305	0.270	0.260
0.1207	.....	0.693	0.670	0.636	0.562
0.2231	4.082	3.345	2.856	2.604	2.355
0.3623	7.521	6.181	5.502	5.024	4.742
			band II		
0.0675	0.339	0.225	0.170	0.130	0.090
0.1207	.....	0.465	0.369	0.303	0.253
0.2231	1.523	1.206	1.072	0.0864	0.076
0.3623	.....	2.305	1.818	1.703	1.430

Table IV: Absorbance Per cm Cell Length for Overtone Transition

conc. at 25° moles/liter	0°	15°	25°	35°	45°
		2,6-Di<u>iso</u>propylphenol			
0.0556	0.152	0.150	0.148	0.145	0.145
0.1158	0.330	0.325	0.317	0.312	0.307
0.2423	0.598	0.595	0.590	0.590	0.573
0.4309	1.07	1.05	1.05	1.05	1.05
0.5307	1.28	1.27	1.27	1.26	1.26
0.6523	1.53	1.53	1.55	1.55	1.50
0.8430	1.97	2.00	2.00	2.00	2.00
1.2758	2.42	2.45	2.47	2.50	2.50
1.4688	2.65	2.70	2.75	2.80	2.80
		2-methyl-6-<u>tert</u>-butylphenol			
0.0707	0.208	0.200	0.195	0.185	0.184
0.1458	0.398	0.384	0.373	0.360	0.350
0.1830	0.545	0.515	0.500	0.486	0.466
0.3906	1.08	1.00	1.02	1.00	0.950
0.4928	1.30	1.25	1.28	1.23	1.17
0.9667	2.27	2.18	2.18	2.14	2.10
1.2841	2.82	2.77	2.72	2.68	2.65
1.4570	3.11	3.10	3.03	2.95	2.95
1.4771	3.16	3.09	3.06	3.05	3.03
		2-<u>iso</u>propylphenol			
0.0477	0.147	0.147	0.147	0.146	0.144
0.0919	0.267	0.275	0.274	0.266	0.266
0.0994	0.266	0.274	0.275	0.279	0.278
0.1451	0.384	0.400	0.404	0.404	0.404
0.1767	0.455	0.427	0.475	0.481	0.481
0.2471	0.525	0.576	0.600	0.614	0.623
0.2920	0.577	0.638	0.676	0.696	0.715
0.3904	0.695	0.776	0.835	0.897	0.890
		2-<u>tert</u>-butylphenol			
0.0412	0.136	0.136	0.134	0.132	0.130
0.0460	0.158	0.155	0.150	0.148	0.145
0.0719	0.235	0.228	0.226	0.222	0.220
0.1438	0.458	0.445	0.443	0.440	0.435
0.2190	0.656	0.646	0.640	0.641	0.637
0.2470	0.745	0.747	0.738	0.740	0.743
0.3613	0.925	0.936	0.942	0.951	0.948
0.4719	1.24	1.25	1.25	1.22	1.22

RESULTS AND DISCUSSION

Stoichiometry Determinations

The values of $A_f/A_o^{\underline{n}}$ for $\underline{n}$ = 1,2,3 for all concentrations at all temperatures as well as the average values over the concentrations at each temperature are presented in Tables V - VII. As stated in the introduction the value of $\underline{n}$ which gives the most nearly constant $A_f/A_o^{\underline{n}}$ ratio is selected as the number of alcohol molecules associating to form the complex. Note that if $\underline{n}$ is too small the value of this ratio increases as concentration increases and if $\underline{n}$ is too large the ratio decreases as concentration increases. The probable error in these averages was calculated at the ninty percent confidence level. The criterion used to select the $\underline{n}$ giving the most constant value of the $A_f/A_o^{\underline{n}}$ ratio was the smallest per cent probable error in averages, (probable error/average) x 100, at a given temperature for a given compound. These averages, probable error in averages and percent probable errors in averages,(probable error/averages) x 100, are shown in Tables IX-XII.

Table XIII shows the values of $\underline{n}$ as determined by the slope of Ln A_f vs. Ln A_o plots. The 2-*tert*-butylphenol and the 2-methyl-6-*tert*-butylphenol systems have a slope ($\underline{n}$) equal to 2 within the 90 percent confidence probable error limits. The value of $\underline{n}$ for 2,6-di*iso*propylphenol is around 2.5. The slope is near 3 for 2-*iso*propylphenol at 0°C and near 2.5 at 45°C.

These calculations seem to indicate that the $\underline{n}$ determined from the $A_f/A_o^{\underline{n}}$ ratio was 2 within the probable error limits in every case except for the 2-*iso*propylphenol where for bands I and II it was found to be 3.

The slopes in Table XIII for 2-isopropylphenol therefore suggest that trimers are probably the major contributor to the band at 0°C and that trimers and dimers are probably both contributing at the higher temperatures. These data seem to indicate that for 2-isopropylphenol in carbon tetrachloride no single stoichiometry occurs and that probably monomer is in equilibrium with dimers and trimers.

Table V: Ratio of A_f/A_o^n for 2,6-di*iso*propylphenol

T(°C)	C(M)	A_f	A_o	A_f/A_o	A_f/A_o^2	A_f/A_o^3
0	0.6713	13.7	1.53	8.95	5.85	3.82
	0.8681	26.0	1.97	13.20	6.70	3.40
	1.3147	39.4	2.43	16.21	6.67	2.74
	1.5146	54.4	2.65	20.53	7.75	2.92
			ave.	14.72	6.74	3.22
15	0.6599	12.7	1.53	8.30	5.43	3.55
	0.8530	23.0	2.00	11.50	5.75	2.88
	1.2914	37.3	2.45	15.22	6.21	2.53
	1.4870	49.8	2.70	18.44	6.83	2.52
			ave.	13.37	6.06	2.87
25	0.6523	10.7	1.55	6.90	4.45	2.87
	0.8430	21.2	2.00	10.60	5.30	2.65
	1.2757	34.0	2.47	13.77	5.58	2.26
	1.4688	45.6	2.75	16.58	6.03	2.19
			ave.	11.96	5.34	2.49
35	0.6447	8.6	1.55	5.55	3.58	2.31
	0.8380	19.3	2.00	9.65	4.83	2.41
	1.2602	31.8	2.50	12.72	5.09	2.04
	1.4506	43.6	2.80	15.57	5.56	1.99
			ave.	10.87	4.77	2.19
45	0.6371	8.3	1.50	5.53	3.69	2.46
	0.8229	17.9	2.00	8.95	4.48	2.24
	1.2448	31.0	2.50	12.40	4.96	1.98
	1.4322	41.5	2.80	14.82	5.92	2.11
			ave.	10.43	4.76	2.19

Table VI: Ratio of A_f/A_o^n for 2-methyl-6-*tert*-butylphenol

T(°C)	C(M)	A_f	A_o	A_f/A_o	A_f/A_o^2	A_f/A_o^3
0	0.9895	27.6	2.27	12.16	5.36	2.36
	1.3228	43.3	2.82	15.35	5.44	1.93
	1.5017	52.8	3.11	16.98	5.46	1.76
	1.5149	53.4	3.16	16.90	5.35	1.69
			ave.	15.35	5.40	1.94
15	0.9781	25.5	2.18	11.70	5.37	2.46
	1.2995	38.7	2.77	13.97	5.04	1.82
	1.4749	47.7	3.10	15.39	4.96	1.60
	1.4954	49.0	3.09	15.86	5.13	1.66
			ave.	14.23	5.12	1.89
25	0.9667	23.0	2.18	10.23	4.85	2.22
	1.2841	37.3	2.72	12.91	5.04	1.85
	1.4570	45.5	3.03	14.41	4.96	1.64
	1.4771	46.5	3.06	14.46	4.97	1.62
			ave.	13.62	4.95	1.83
35	0.9553	22.3	2.14	10.23	4.69	2.15
	1.2687	34.6	2.68	12.91	4.82	1.80
	1.4391	42.5	2.95	14.41	4.88	1.65
	1.4588	44.1	3.05	14.46	4.74	1.55
			ave.	13.00	4.78	1.79
45	0.9438	22.8	2.10	10.86	5.17	2.46
	1.2533	34.6	2.65	13.06	4.93	1.86
	1.4213	41.5	2.95	14.07	4.77	1.62
	1.4406	42.5	3.03	14.03	4.63	1.53
			ave.	13.00	4.88	1.88

Table VII: Ratio of A_f/A_o^n for 2-isopropylphenol

				band I		
T(°C)	C(M)	A_f	A_o	A_f/A_o	A_f/A_o^2	A_f/A_o^3
0	0.1022	0.645	0.266	2.43	9.12	34.3
	0.1492	.....	0.384	....	....	....
	0.2533	4.87	0.525	9.276	17.66	33.6
	0.3004	7.15	0.577	12.39	21.47	37.2
	0.4018	10.00	0.695	14.39	20.71	29.8
			ave.	9.62	17.24	33.7
15	0.1011	0.544	0.274	1.985	7.25	26.44
	0.1476	1.258	0.400	3.145	7.86	19.65
	0.2505	4.23	0.576	7.344	12.75	22.14
	0.2971	6.27	0.638	9.828	15.40	24.14
	0.3972	8.70	0.776	11.21	14.45	18.62
			ave.	6.70	11.54	22.20
25	0.0994	0.483	0.275	1.756	6.38	23.22
	0.1451	0.985	0.404	2.438	6.04	14.94
	0.2471	3.67	0.600	6.117	10.20	17.00
	0.2920	5.44	0.676	8.047	11.90	17.60
	0.3904	7.87	0.835	9.425	11.29	13.52
			ave.	5.557	9.16	17.26
35	0.0976	0.447	0.279	1.602	5.74	20.57
	0.1434	.....	0.404	......	.....	.....
	0.2434	3.50	0.614	5.70	9.28	15.11
	0.2886	5.13	0.696	7.37	10.59	15.21
	0.3859	7.48	0.897	8.34	9.30	10.36
			ave.	5.75	8.73	15.31
45	0.0972	....	0.278	....	.....	.....
	0.1418	0.970	0.404	2.40	5.94	14.71
	0.2415	3.07	0.623	4.93	7.91	12.70
	0.2852	4.65	0.715	6.50	9.09	12.71
	0.3813	6.84	0.890	7.69	8.63	9.70
			ave.	5.38	7.90	12.46

Table VII con't   Ratio of A_f/A_o^n for 2-isopropylphenol

band II

T(°C)	C(M)	A_f	A_o	A_f/A_o	A_f/A_o^2	A_f/A_o^3
0	0.1022	0.745	0.266	2.84	10.66	40.08
	0.1492	....	0.384	....	.....	.....
	0.2533	5.90	0.525	11.24	21.41	40.78
	0.3004	8.48	0.577	14.70	25.47	44.14
	0.4018	12.01	0.695	17.28	24.86	35.77
			ave.	11.52	20.60	40.20
15	0.1011	0.556	0.274	2.029	7.405	27.02
	0.1476	1.331	0.400	3.328	8.320	20.80
	0.2505	4.56	0.576	7.917	13.74	23.85
	0.2971	6.72	0.638	10.533	16.51	25.87
	0.3972	9.25	0.776	11.92	15.36	19.79
			ave.	7.14	12.27	23.47
25	0.0994	0.413	0.275	1.502	5.462	19.86
	0.1451	1.062	0.404	2.629	6.51	16.11
	0.2471	3.10	0.600	5.167	8.12	14.35
	0.2920	4.90	0.676	7.249	10.72	15.86
	0.3904	7.57	0.835	9.066	10.86	13.01
			ave.	5.123	8.33	15.84
35	0.0976	0.362	0.279	1.297	4.65	16.67
	0.1434	0.897	0.404	2.220	5.50	13.60
	0.2434	2.99	0.614	4.870	7.93	12.92
	0.2886	4.44	0.696	6.379	9.15	13.15
	0.3859	6.61	0.897	7.369	8.22	9.16
			ave.	4.427	7.09	13.10
45	0.0972	....	0.278	......	......	.....
	0.1418	0.816	0.404	2.020	5.00	12.38
	0.2415	2.53	0.623	4.061	6.52	10.47
	0.2852	3.78	0.715	5.287	7.39	10.32
	0.3813	5.69	0.890	6.393	7.18	8.07
			ave.	4.44	6.02	10.31

Table VIII: Ratio of A_f/A_o^n for 2-<u>tert</u>-butylphenol

				band I		
T(°C)	C(M)	A_f	A_o	A_f/A_o	A_f/A_o^2	A_f/A_o^3
0	0.0739	0.465	0.235	1.978	8.417	35.82
	0.1479	.....	0.458	.....	.....	.....
	0.2253	4.08	0.656	6.220	9.48	14.45
	0.3719	7.52	0.925	8.130	8.79	9.50
			ave.	5.443	8.90	19.92
15	0.0731	0.326	0.228	1.430	6.272	28.41
	0.1462	0.693	0.445	1.557	3.499	7.86
	0.2228	3.35	0.646	5.186	8.028	12.43
	0.3677	6.18	0.936	6.603	7.05	7.53
			ave.	3.694	6.21	14.06
25	0.0719	0.305	0.226	1.350	5.97	26.42
	0.1438	0.670	0.443	1.512	3.41	7.70
	0.2190	2.788	0.640	4.36	6.81	10.64
	0.3613	5.502	0.942	5.84	6.20	6.58
			ave.	3.27	5.59	12.84
35	0.0710	0.270	0.222	1.216	5.48	24.68
	0.1421	0.636	0.440	1.445	3.28	7.46
	0.2165	2.601	0.641	4.058	6.33	9.88
	0.3570	5.024	0.951	5.283	5.55	5.84
			ave.	3.00	5.16	11.97
45	0.0702	0.260	0.220	1.182	5.37	24.42
	0.1405	0.562	0.435	1.292	2.97	6.83
	0.2139	2.36	0.637	3.742	5.87	9.22
	0.3528	4.74	0.948	5.000	5.27	5.56
			ave.	2.80	4.86	11.51

Table VIII con't Ratio of A_f/A_o^n for 2-tert-butylphenol

band II

T(°C)	C(M)	A_f	A_o	A_f/A_o	A_f/A_o^2	A_f/A_o^3
0	0.0739	0.339	0.235	1.443	6.140	26.1
	0.1479	.....	0.458	.....	.....	....
	0.2253	1.52	0.656	2.317	3.532	5.38
	0.3719	....	0.925	.....	.....	....
			ave.	1.88	4.83	15.76
15	0.0731	0.225	0.228	0.987	4.33	18.99
	0.1462	0.465	0.445	1.045	2.35	5.28
	0.2228	1.21	0.646	1.873	2.90	4.49
	0.3677	2.31	0.936	2.468	2.63	2.81
			ave.	1.59	3.05	7.89
25	0.0719	0.170	0.226	0.752	3.33	14.73
	0.1438	0.369	0.443	0.833	1.88	4.24
	0.2190	1.072	0.640	1.675	2.62	4.09
	0.3613	1.818	0.942	1.932	2.05	2.18
			ave.	1.30	2.47	6.31
35	0.0710	0.130	0.222	0.586	2.64	11.88
	0.1421	0.330	0.440	0.750	1.71	3.88
	0.2165	0.864	0.641	1.320	2.06	3.21
	0.3570	1.704	0.951	1.792	1.88	1.98
			ave.	1.11	2.07	5.23
45	0.0702	0.090	0.220	0.409	1.86	8.45
	0.1405	0.253	0.435	0.582	1.34	3.07
	0.2139	0.756	0.637	1.187	1.86	2.92
	0.3528	1.430	0.948	1.508	1.59	1.68
			ave.	0.922	1.76	4.03

Table IX: Average Values,# Probable Errors in Average Values, and Percent Probable Errors in Average Values of A_f/A_o^n for 2-methyl-6-*tert*-butylphenol

T(°C)		A_f/A_o	A_f/A_o^2	A_f/A_o^3	Probable *n*
0	ave.	15.35	5.40	1.94	
	*P.E. in ave.	2.79	0.0647	0.353	
	P.E./ave. x 100	18.2	1.20	18.2	2
15		14.23	5.12	1.89	
		2.153	0.213	0.454	
		15.1	4.16	24.0	2
25		13.62	4.95	1.83	
		2.34	0.092	0.287	
		17.2	1.87	15.7	2
35		13.00	4.78	1.79	
		2.330	0.099	0.307	
		17.9	2.07	17.2	2
45		13.01	4.88	1.88	
		1.753	0.264	0.485	
		13.5	5.40	25.8	2

* Probable error calculated at 90% confidence

Table VI

Table X: Average Values,# Probable Errors in Average Values, and Percent Probable Errors in Average Values of A_f/A_o^n for 2,6-d<u>iiso</u>propylphenol

T(°C)		A_f/A_o	A_f/A_o^2	A_f/A_o^3	Probable <u>n</u>
0	ave.	14.72	6.74	3.22	
	*P.E. in Ave.	4.98	0.912	0.563	
	P.E./ave. x 100	33.8	13.5	17.5	2
15		13.37	6.06	2.87	
		5.17	0.713	0.563	
		38.7	11.8	19.6	2
25		11.96	5.34	2.49	
		4.894	0.777	0.372	
		40.9	14.6	14.9	2
35		10.87	4.77	2.19	
		5.03	0.993	0.236	
		46.3	20.8	10.8	3
45		10.43	4.76	2.09	
		4.56	1.10	0.236	
		43.7	23.0	10.8	3

* Probable error calculated at 90% confidence level

\# Table V

Table XI: Average Values#, Probable Errors in Average Values, and Percent Probable Error in Average Values of A_f/A_o^n for 2-isopropylphenol

T(°C)		A_f/A_o	A_f/A_o^2	A_f/A_o^3	Probable n
			band I		
0	ave.	9.62	17.24	33.73	
	*P.E. in ave.	6.14	6.025	3.26	
	P.E./ave. x 100	63.8	34.9	9.67	3
15		6.70	11.54	22.20	
		3.85	5.532	3.06	
		57.5	47.9	13.8	3
25		5.557	9.16	17.26	
		3.28	2.651	3.51	
		59.0	28.9	20.3	3
35		5.75	8.73	15.31	
		3.49	2.45	4.89	
		60.7	28.0	32.0	2
45		5.38	7.90	12.46	
		2.66	1.636	2.42	
		49.4	20.7	19.5	3,2
			band II		
0	ave.	11.52	20.60	40.20	
	* P.E. in ave.	7.41	8.06	4.12	
	P.E./ave. x 100	64.3	39.1	10.2	3
15		7.14	12.27	23.47	
		4.14	3.95	2.40	
		58.0	32.2	10.2	3
25		5.123	8.33	15.84	
		2.98	2.44	2.45	
		58.3	29.3	15.5	3
35		4.427	7.09	13.10	
		2.50	1.82	2.56	
		56.5	25.7	19.5	3
45		4.44	6.02	10.31	
		2.20	1.44	2.00	
		49.5	23.9	19.4	3

* Probable error calculated at 90% confidence level

\# Table VII

Table XII: Average Values,# Probable Errors in Average Values, and Percent Probable Errors in Average Values of A_f/A_o^n for 2-tert-butylphenol

T(°C)		A_f/A_o	A_f/A_o^2	A_f/A_o^3	Probable n
			band I		
0	ave.	5.443	8.90	19.92	
	*P.E. in ave.	5.294	0.892	23.44	
	P.E./ave. x 100	97.3	10.02	117.7	2
15		3.694	6.21	14.06	
		3.031	2.294	11.51	
		82.1	36.9	81.9	2
25		3.27	5.59	12.84	
		2.59	1.765	10.77	
		79.1	31.6	83.9	2
35		3.00	5.16	11.97	
		2.34	1.671	10.12	
		78.0	32.4	84.5	2
45		2.80	4.86	11.51	
		2.20	1.518	10.26	
		78.5	4.86	89.1	2
			band II		
0	Ave.	1.88	4.83	15.76	
	*P.E. in ave.	2.75	8.26	65.19	
	P.E./ave. x 100	146.3	171.0	414.0	2
15		1.59	3.05	7.89	
		0.833	1.03	8.77	
		52.1	33.8	111.2	2
25		1.30	2.47	6.31	
		0.697	.78	6.68	
		53.7	31.2	105.6	2
35		1.11	2.07	5.23	
		0.647	0.475	5.29	
		57.8	22.9	101.1	2
45		0.922	1.76	4.03	
		0.809	0.322	3.59	
		87.7	18.3	89.1	2

* Probable error calculated at 90% confidence level

Table VIII

Table XIII: Least Squares Treatment of Ln A_f vs. Ln A_o

2,6-diisopropylphenol

T(°C)	Slope*	Intercept*
0	2.4227 ± 0.4144	1.5901 ± 0.3195
15	2.3793 ± 0.2457	1.5119 ± 0.1923
25	2.4980 ± 0.1986	1.2896 ± 0.1574
35	2.7013 ± 0.4262	1.0084 ± 0.3418
45	2.5707 ± 0.0984	1.0834 ± 0.7585
all	2.4936 ± 0.3030	1.6860 ± 0.1385
	2-methyl-6-tert-butylphenol	
0	2.0248 ± 0.1366	1.6610 ± 0.1426
15	1.8237 ± 0.2089	1.8130 ± 0.2140
25	2.0738 ± 0.1606	1.5254 ± 0.1624
35	1.9585 ± 0.1511	1.6153 ± 0.1504
45	1.7253 ± 0.1457	1.8514 ± 0.1439
all	1.9249 ± 0.1382	1.6860 ± 0.1335
	2-isopropylphenol	
	band I	
0	2.9292 ± 0.4289	3.4643 ± 0.3460
15	2.8021 ± 0.3897	2.9546 ± 0.3062
25	2.6610 ± 0.4281	2.6084 ± 0.3208
35	2.4876 ± 0.4547	2.4139 ± 0.3224
45	2.5265 ± 0.4500	2.2946 ± 0.2433
all	2.4461 ± 0.2362	2.4880 ± 0.1794
	band II	
0	2.9547 ± 0.4179	3.6601 ± 0.3371
15	2.8441 ± 0.3903	3.0405 ± 0.3066
25	2.6736 ± 0.1951	2.5381 ± 0.1491
35	2.5883 ± 0.2964	2.2963 ± 0.2230
45	2.5034 ± 0.3738	2.0946 ± 0.2023
all	2.4040 ± 0.3282	2.3741 ± 0.2518

Table XIII: Cont.

2-*tert*-butylphenol

T(°C)	Slope*	Intercept*
	band I	
15	2.1864 ± 1.1946	1.9112 ± 1.0409
25	2.1088 ± 1.0382	1.7657 ± 0.9107
35	2.0921 ± 0.9466	1.6775 ± 0.8386
45	2.0684 ± 1.0163	1.5966 ± 0.9078
all	2.0977 ± 0.2359	1.7636 ± 0.2089
	band II	
15	1.6763 ± 0.6238	0.8613 ± 0.5435
25	1.7210 ± 0.6591	0.6825 ± 0.5782
35	1.8095 ± 0.6118	0.5643 ± 0.5420
45	1.9459 ± 0.5116	0.4608 ± 0.4570
all	1.8815 ± 0.2133	0.7025 ± 0.1762

* Probable errors calculated at 90% confidence level

Determination of the Absorption Coefficients

Figures 5 through 8 are plots of overtone absorbance per cm path length *vs.* molar concentration of the phenols at 0, 25, and 45°C. Note that deviation from Beer's law due to association occurs at lower concentration for the 2-*iso*propylphenol and 2-*tert*-butylphenol (Figures 7-8) than for 2,6-di*iso*propylphenol and 2-methyl-6-*tert*-butylphenol (Figures 5-6). In the least squares analysis of plots of absorbance *vs.* concentration to determine the monomer absorption coefficient, a_m, the three lowest concentration in Table IV were used with their corresponding absorbances for 2-*tert*-butylphenol while the lowest five concentrations were used for 2,6-di*iso*propylphenol and 2-methyl-6-*tert*-butylphenol. For 2-*iso*propylphenol the lowest concentration data were used to calculate the monomer absorption coefficient. The monomer absorption coefficient, a_m, for the 7100 cm^{-1} band was used in the calculation of apparent monomer concentration, $c_1 = A_o/a_m$ for use in Ln $(c-c_1)$ *vs.* Ln c_1 plots and the Masschelein calculation to be discussed in the following section of the thesis.

The monomer absorption coefficients, obtained from the least squares analysis of absorbance *vs.* concentration plots, are shown in Table XIV for each temperature. Also included in Table XIV for each compound are the absorption coefficient obtained using all data at all temperatures, a_{mI}, and the average value of the temperature dependent absorption coefficients.

Note that for 2-*tert*-butylphenol and for 2-methyl-6-*tert*-butylphenol the value of the absorption coefficient decreases as the temperature

Figure 5 Plot of Absorbance of 7100 cm^{-1} band *vs.* concentration for 2,6-di*iso*propylphenol

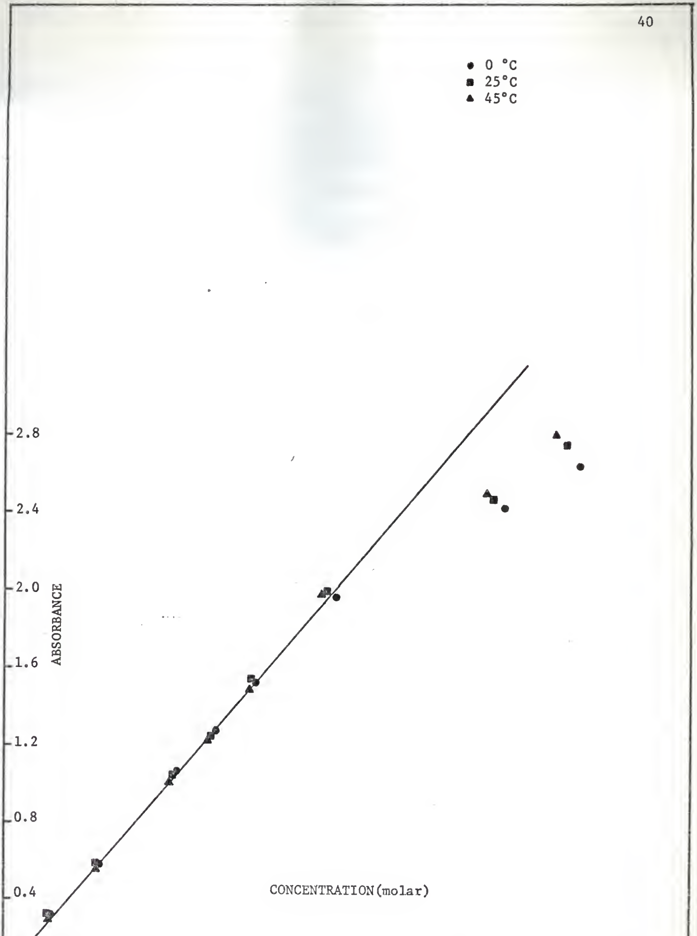

0 °C
25°C
45°C
ABSORBANCE
2.8
2.4
2.0
1.6
1.2
0.8
0.4
CONCENTRATION(molar)
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6

Figure 6 Plot of Absorbance of 7100 cm^{-1} band vs. concentration for 2-methyl-6-*tert*-butylphenol

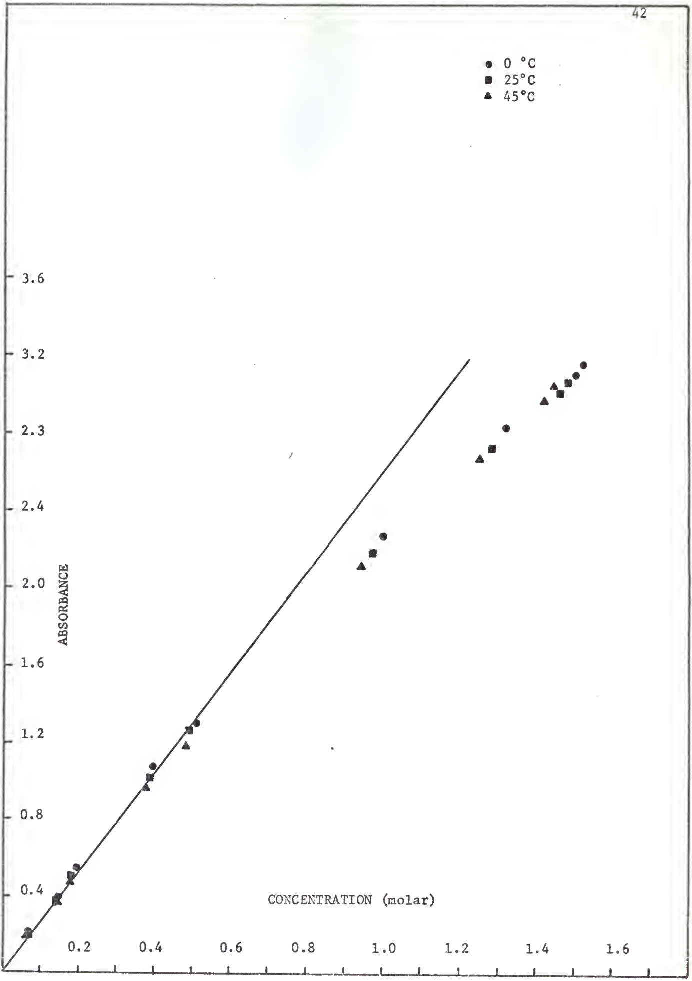

0 °C
25°C
45°C
3.6
3.2
2.3
2.4
2.0
1.6
1.2
0.8
0.4
ABSORBANCE
CONCENTRATION (molar)
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6

Figure 7 Plot of Absorbance of 7100 cm^{-1} band vs. concentration for 2-isopropylphenol

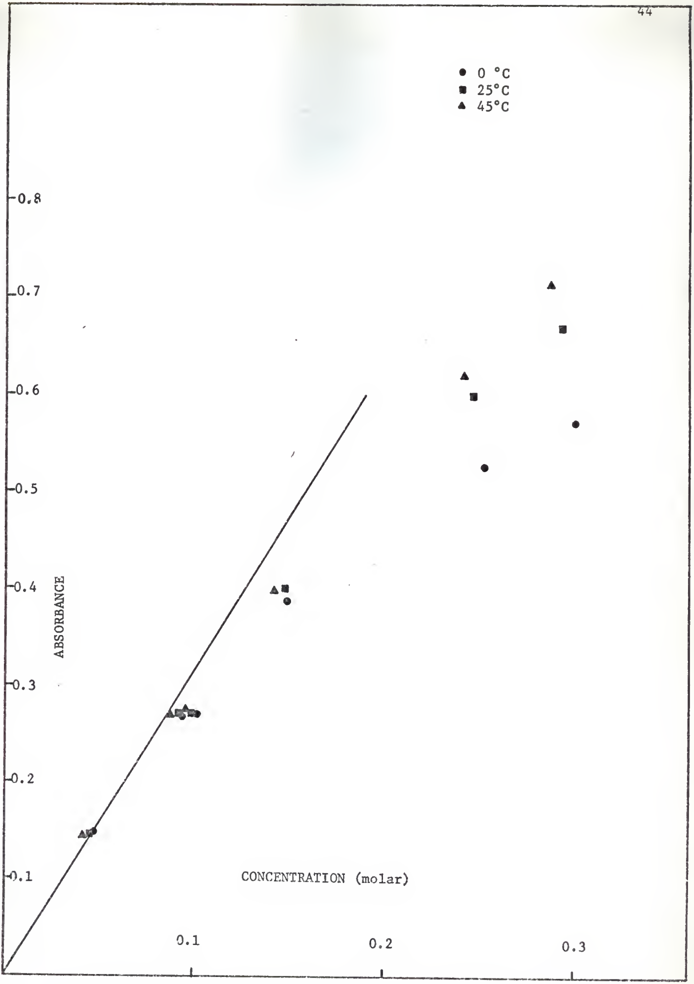
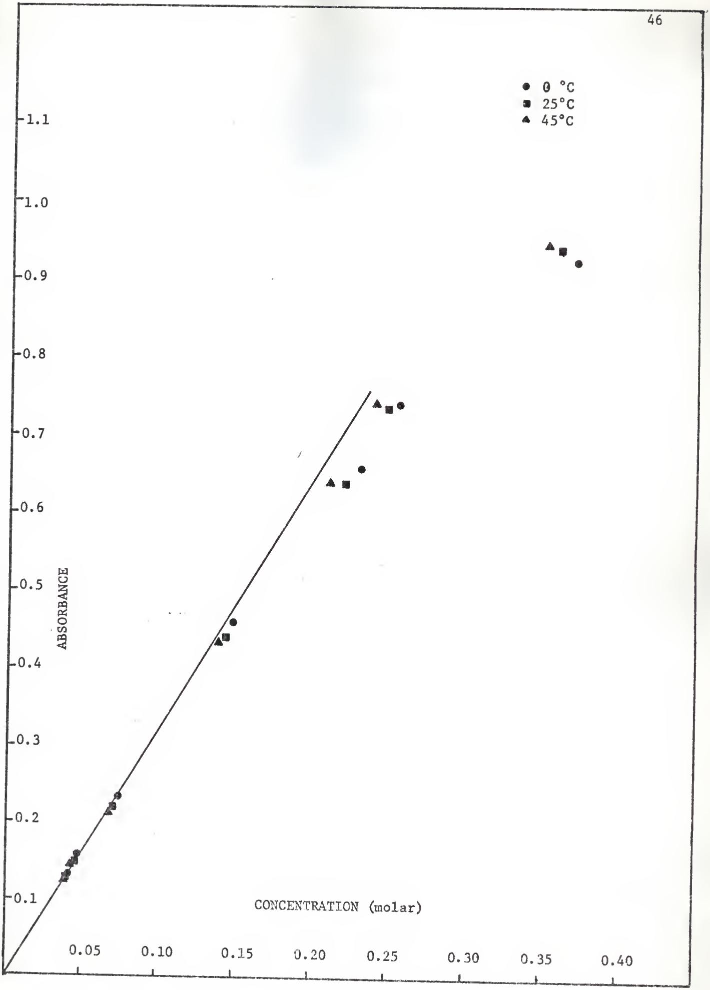

0 °C
25°C
45°C
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
ABSORBANCE
CONCENTRATION (molar)
0.1
0.2
0.3

Figure 8 Plot of Absorbance of 7100 cm^{-1} band *vs*. concentration for 2-*tert*-butylphenol



● 0 °C
■ 25°C
▲ 45°C
ABSORBANCE
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
CONCENTRATION (molar)
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40

increases while it increases for 2-*iso*propylphenol and 2,6-di*iso*propylphenol. There is no apparent explanation for this abnormality.

Table XV shows the values of $R \times 10^3$ defined by Swenson (6) as R = (fraction change in absorption coefficient)/(temperature change in °C).

Table XVI shows the absorption coefficients of the complex, a_f, calculated from the absorbance per unit path length of the fundamental band divided by the concentration of the complex which was determined by substracting the monomer concentration c_1 from the total concentration $\underline{c}$. The values listed are averages over the concentration ranges shown for each compound. The results of this calculation may be in error due to the OH end groups of the complex which may contribute to the absorbance used to calculate $\underline{c_1}$. This causes $\underline{c_1}$ to be too large and thus makes $(c-c_1)$ too small and $\underline{a_f}$, the absorption coefficient of the complex too large. The concentration of monomer $\underline{c_1}$ was calculated two ways: one was with the temperature dependent monomer absorption coefficient (a_m) and the other was with the temperature independent monomer absorption coefficient (a_{mI}). In addition Table XVI contains a_f values calculated using the results of the Masschelein calculation described in the next section to correct for errors in $(c-c_1)$ caused by contributions to the 7100 cm^{-1} band absorbance from the OH end group of the complex.

Masschelein Calculation

To gain an estimate of the magnitude of the OH end group contribution of the complex to the overtone band intensity the technique of Masschelein (9) was used. The results are shown in Table XVII along with the slopes from the Ln A_f vs. Ln A_o and Ln $(c-c_1)$ vs. Ln c_1 plots. It is seen that the free OH end groups of the complex may cause spurious results for $\underline{n}$ determined from Ln $(c-c_1)$ vs. Ln c_1 plots. The OH end groups of the complex

Table XIV: Monomer Absorption Coefficients (cm^{-1} $mole^{-1}$ liter) from 7100 cm^{-1} band

T(°C)	2-*iso*propylphenol*#	2-*tert*-butylphenol*
0	2.9982	3.2250 ± 0.1388
15	3.0478	3.1903 ± 0.1741
25	3.0817	3.1931 ± 0.1149
35	3.0953	3.1774 ± 0.1253
45	3.0877	3.1722 ± 0.0952
a_{mI}	3.0621	3.1842 ± 0.0299
ave.	3.0621	3.1896 ± 0.0592

T(°C)	2,6-di*iso*propylphenol*	2-methyl-6-*tert*-butylphenol*
0	2.3965 ± 0.0344	2.6428 ± 0.1056
15	2.3892 ± 0.0444	2.5246 ± 0.0503
25	2.4146 ± 0.0389	2.5918 ± 0.0512
35	2.4390 ± 0.0612	2.5576 ± 0.0513
45	2.4587 ± 0.0572	2.4663 ± 0.0555
a_{mI}	2.4191 ± 0.0196	2.5602 ± 0.0248
ave.	2.4196 ± 0.0215	2.5566 ± 0.0656

*Probable errors calculated at 90% confidence level
#based on lowest concentration only

Table XV: ($R \times 10^3$) Change in absorption Coefficient

2-*iso*propylphenol	2-*tert*-butylphenol
-0.66	0.36

2,6-di*iso*propylphenol	2-methyl-6-*tert*-butylphenol
-0.58	1.48

Table XVI: Absorption Coefficient of the Complex (cm^{-1} $moles^{-1}$ liters) from $3500\ cm^{-1}$ band

$A_f/(c-c_1) = a_f$

T(°C)	Conc. (M) Range	Using Temp. Independent a_{mI}		Using Temp. Dependent a_m		Using Masschelein Results*	
2-methyl-6-*tert*-butylphenol							
0		189.3		165.3		119.0	
15		176.0		188.3		125.0	
25	1.2841-1.4771	167.0		158.1		111.0	
35		157.0		157.2		110.0	
45		159.7		192.7		122.0	
2,6-di*iso*propylphenol							
0		129.3		132.0		82.4	
15		135.2		139.9		82.3	
25	1.2758-1.4688	136.7		144.5		80.2	
35		146.0		139.7		77.2	
45		151.3		138.7		75.7	
2-*iso*propylphenol		band I	band II	band I	band II	band I	band II
0		60.52	72.21	62.5	74.7	62.5	74.7
15		65.54	70.04	67.7	72.3	67.7	72.3
25	0.2920-0.3904	71.63	66.55	70.8	65.8	70.8	65.8
35		82.05	71.75	79.5	69.5	79.5	69.5
45		82.67	67.92	84.0	69.0	84.0	69.0
2-*tert*-butylphenol							
0		92.4	--	83.37	--	65.9	--
15		83.87	31.48	83.18	31.1	59.5	22.2
25	0.3613	84.00	27.76	82.99	27.3	57.2	18.9
35		86.17	29.23	87.07	29.5	57.1	19.2
45		86.1	26.0	87.78	26.5	56.4	17.0

*See page 47 for discussion of Masschelein results

Table XVII: Results for n from the Masschelein Plots

T(°C)	Ln A_f vs. Ln A_o n	Ln($c-c_1$) vs. Ln c_1^+ n	x = 1.0 n	0.9 n	0.8 n	0.7 n
2,6-diisopropylphenol*						
0	2.423 ± 0.414	4.732 ± 3.357	4.956 ± 3.530	3.242 ± 2.049	2.609 ± 1.478	2.263 ± 1.163
15	2.379 ± 0.246	5.209 ± 5.581	5.759 ± 6.680	3.278 ± 2.662	2.568 ± 1.778	2.206 ± 1.348
25	2.498 ± 0.199	6.811 ± 5.437	6.155 ± 2.087	3.160 ± 2.087	2.444 ± 1.380	2.093 ± 1.039
35	2.701 ± 0.426	9.144 ± 6.935	6.634 ± 5.151	3.223 ± 2.059	2.475 ± 1.361	2.114 ± 1.024
45	2.571 ± 0.098	7.976 ± 1.766	4.588 ± 8.156	2.702 ± 2.575	2.161 ± 1.645	1.887 ± 1.220
2-methyl-6-tert-butylphenol*						
0	2.025 ± 0.137	3.147 ± 0.666	2.819 ± 0.491	2.218 ± 0.297	1.918 ± 0.212	1.737 ± 0.165
15	1.824 ± 0.209	2.223 ± 0.491	3.211 ± 0.941	2.316 ± 0.542	1.941 ± 0.385	1.733 ± 0.299
25	2.074 ± 0.161	2.632 ± 0.473	2.526 ± 0.432	2.004 ± 0.253	1.749 ± 0.177	1.598 ± 0.136
35	1.959 ± 0.151	----- -----	3.035 ± 1.290	2.274 ± 0.811	1.931 ± 0.595	1.734 ± 0.471
45	1.725 ± 0.146	----- -----	2.417 ± 0.858	1.825 ± 0.503	1.584 ± 0.357	1.452 ± 0.277
2-tert-butylphenol*						
0	---- ----	4.138 ± 1.090	3.194 ± 0.708	1.861 ± 0.739	1.574 ± 0.563	1.434 ± 0.452
15	2.186 ± 1.195	2.584 ± 0.434	2.675 ± 0.692	1.711 ± 0.592	1.473 ± 0.445	1.356 ± 0.354
25	2.109 ± 1.038	2.898 ± 0.739	2.861 ± 0.669	1.699 ± 0.563	1.454 ± 0.411	1.338 ± 0.322
35	2.092 ± 0.947	2.706 ± 1.021	1.733 ± 0.257	1.236 ± 1.021	1.149 ± 0.666	1.110 ± 0.497
45	2.068 ± 1.016	2.262 ± 1.808	2.835 ± 0.890	1.597 ± 0.578	1.376 ± 0.398	1.276 ± 0.304

Table XVII continued

T(°C)	Ln A_f vs. Ln A_o	Ln$(c-c_1)$ vs. Ln c_1 +	X = 1.0 n	0.9 n	0.8 n
2-isopropylphenol*					
			X = 1.0	0.95	0.90
0	2.929 ± 0.429	2.780 ± 0.840	2.779 ± 0.705	2.524 ± 0.615	2.338 ± 0.548
15	2.802 ± 0.390	2.596 ± 0.741	2.560 ± 0.708	2.283 ± 0.589	2.096 ± 0.510
25	2.661 ± 0.428	2.358 ± 0.675	2.371 ± 0.635	2.093 ± 0.503	1.914 ± 0.422
35	2.448 ± 0.455	2.385 ± 0.389	2.356 ± 0.409	2.023 ± 0.316	1.828 ± 0.259
45	2.527 ± 0.450	2.276 ± 0.457	2.249 ± 0.466	1.925 ± 0.357	1.741 ± 0.294

* Probable errors calculated at 90% confidence

\+ Ln$(c-c_1)$ vs. Ln c_1 is identical to a Masschelein calculation with X = 1.0. Here a_m is used in the Masschelein calculation while a_{mI} was used in the Ln$(c-c_1)$ vs. Ln C_1 so this column and the X = 1.0 column are slightly different.

may cause the Ln $(c-c_1)$ vs. Ln c_1 results for n to be larger than the slope of Ln A_f vs. Ln A_o and the n determined from the A_f/A_o^n results. The three methods of evaluating n for 2-tert-butylphenol and 2-methyl-6-tert-butylphenol are in satisfactory agreement if a Masschelein calculation using X = 0.9 is employed in the Ln $(c-c_1)$ vs. Ln c_1 calculation where X is the fraction of the 7100 cm^{-1} band intensity contributed by monomer. The X value needed to bring Ln $(c-c_1)$ vs. Ln c_1 plots into agreement with the results of Ln A_f vs. Ln A_o plots is approximately 0.8 for 2,6-diisopropylphenol and the X value needed to bring this plot into agreement for 2-isopropylphenol is 1.0. It,therefore, appears that in all of these systems except 2-isopropylphenol the overtone absorbances are affected by some complex OH end group contribution. In all calculations where the free OH absorbance near 7100 cm^{-1} is used to represent monomer concentration this complex OH end group concentration should be considered. Therefore, the absorption coefficient of the complex, a_f, was also calculated using the best value of the Masschelein calculation to correct the monomer concentration obtained from the intensity of the 7100 cm^{-1} band (Table XVI).

Thermodynamics

Figures 9 through 14 are plots of quantities that are proportional to the logarithm of the equilibrium constant vs. 1/T for each of the systems. These quantities are the intercept from the Ln A_f vs. Ln A_o plots, the logarithm of A_f/A_o^2 for all concentrations and for the concentrations giving the best average value of A_f/A_o^2, and the logarithm of A_f/A_o^2 corrected for changes in the absorption coefficients using a_f values calculated using both a_m and a_{mI} without Masschelein X values

Figure 9. Plots to Obtain ΔH for 2,6-di*iso*propylphenol

1) Intercept from Ln A_f *vs.* Ln A_o plots (Table XIII).

2) Logarithm of A_f/A_o^2 average value for all concentrations.

3) Logarithm of A_f/A_o^2 best average value.

4) Logarithm of A_f/A_o^2 average values for all concentrations corrected

for changes in the absorption coefficients using temperature dependent a_m values and a_f values calculated not using Masschelein X values.

5) Logarithm of A_f/A_o^2 average value for all concentrations corrected for changes in the absorption coefficients using temperature independent a_{mI} values and a_f values calculated not using Masschelein X values.

6) Logarithm of A_f/A_o^2 average value for all concentrations corrected for changes in the absorption coefficients using temperature dependent a_m values and a_f values calculated using Masschelein X values.

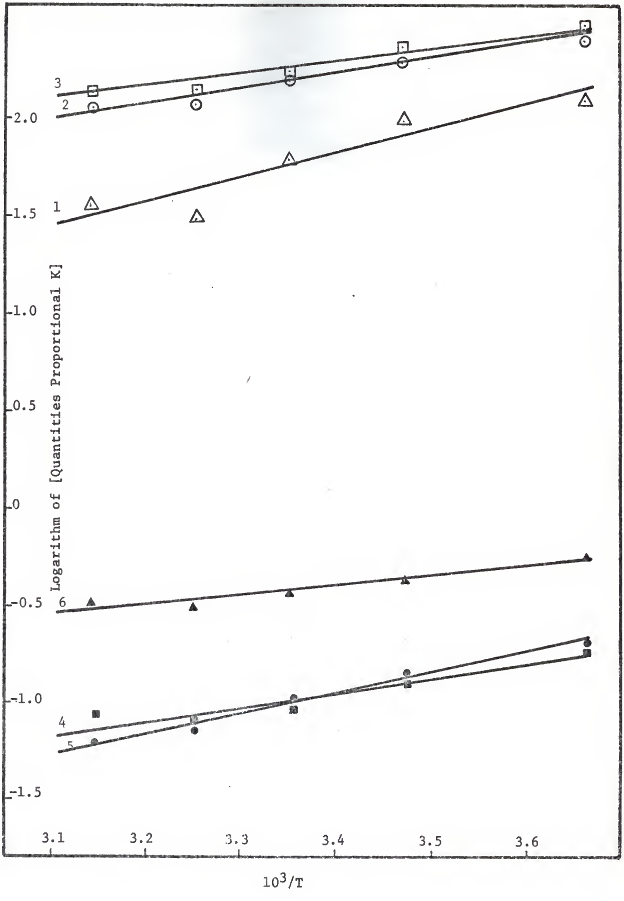

3
2
1
6
4
5
-2.0
-1.5
-1.0
-0.5
0
0.5
1.0
1.5
Logarithm of [Quantities Proportional K]
3.1
3.2
3.3
3.4
3.5
3.6
10^3/T

Figure 10. Plots to Obtain ΔH for 2-methyl-6-*tert*-butylphenol

1) Intercept from Ln A_f *vs*. Ln A_o plots (Table XIII).

2) Logarithm of A_f/A_o^2 average value for all concentrations.

3) Logarithm of A_f/A_o^2 best average value.

4) Logarithm of A_f/A_o^2 average values for all concentrations corrected

   for changes in the absorption coefficients using temperature dependent a_m values and a_f values calculated not using Masschelein X values.

5) Logarithm of A_f/A_o^2 average values for all concentrations corrected for changes in the absorption coefficients using temperature independent a_{mI} values and a_f values calculated not using Masschelein X values.

6) Logarithm of A_f/A_o^2 average value for all concentrations corrected for changes in the absorption coefficients using temperature dependent a_m values and a_f values calculated using Masschelein X values.

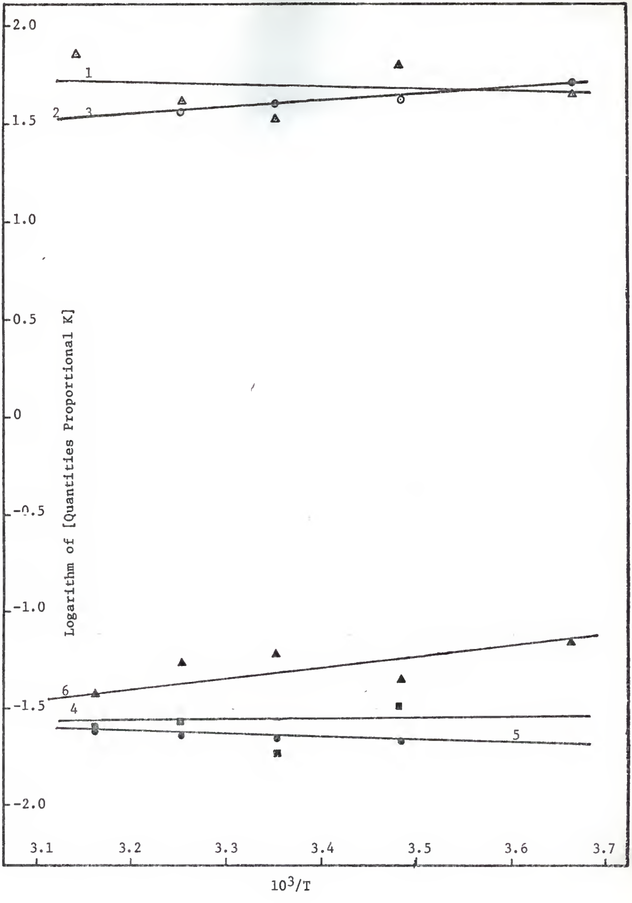

2.0
1.5
1.0
0.5
0
-0.5
-1.0
-1.5
-2.0
Logarithm of [Quantities Proportional K]
1
2
3
4
5
6
3.1
3.2
3.3
3.4
3.5
3.6
3.7
$10^3/T$

Figure 11. Plots to Obtain ΔH from Band I for 2-isopropylphenol

1) Intercept from Ln A_f vs. Ln A_o plots (Table XIII).

2) Logarithm of A_f/A_o^2 average value for all concentrations.

3) Logarithm of A_f/A_o^2 best average value.

4) Logarithm of A_f/A_o^2 average values for all concentrations corrected for changes in the absorption coefficients using temperature dependent a_m values and a_f values calculated not using Masschelein X values.

5) Logarithm of A_f/A_o^2 average value for all concentrations corrected for changes in the absorption coefficients using temperature independent a_{mI} values and a_f values calculated not using Masschelein X values.

6) Logarithm of A_f/A_o^2 average value for all concentrations corrected for changes in the absorption coefficients using temperature dependent a_m values and a_f values calculated using Masschelein X values.

7) Logarithm of A_f/A_o^3 average for all concentrations.

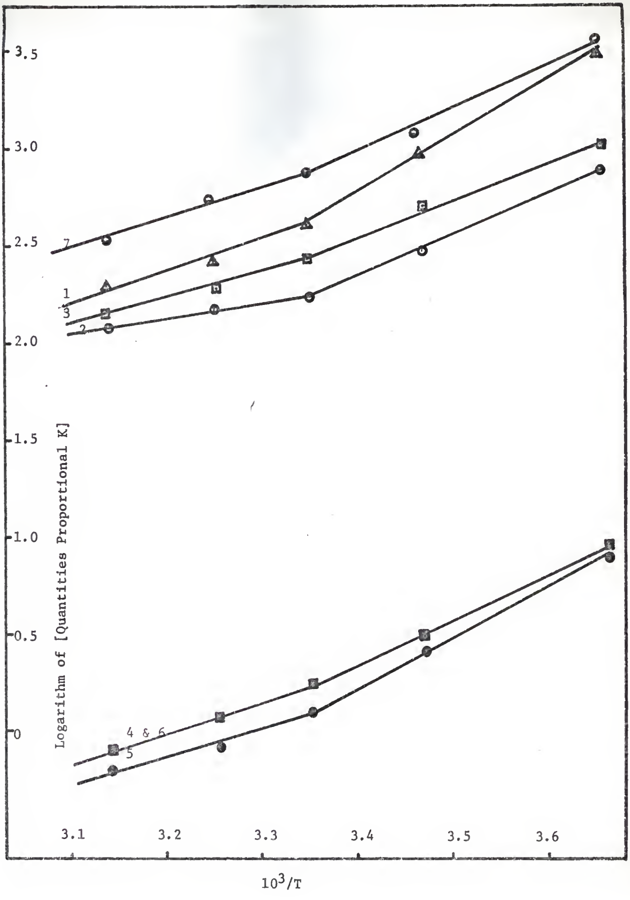

3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
7
1
3
2
4 & 6
5
Logarithm of [Quantities Proportional K]
3.1
3.2
3.3
3.4
3.5
3.6
$10^3/T$

Figure 12. Plots to Obtain ΔH from Band II for 2-*iso*propylphenol

1) Intercept from Ln A_f *vs*. Ln A_o plots (Table XIII).

2) Logarithm of A_f/A_o^2 average value for all concentrations.

3) Logarithm of A_f/A_o^2 best average value.

4) Logarithm of A_f/A_o^2 average values for all concentrations corrected

   for changes in the absorption coefficients using temperature dependent a_m values and a_f values calculated not using Masschelein X values.

5) Logarithm of A_f/A_o^2 average value for all concentrations corrected for changes in the absorption coefficients using temperature independent a_{mI} values and a_f values calculated not using Masschelein X values.

6) Logarithm of A_f/A_o^2 average value for all concentrations corrected for changes in the absorption coefficients using temperature dependent a_m values and a_f values calculated using Masschelein X values.

7) Logarithm of A_f/A_o^3 average value for all concentrations.

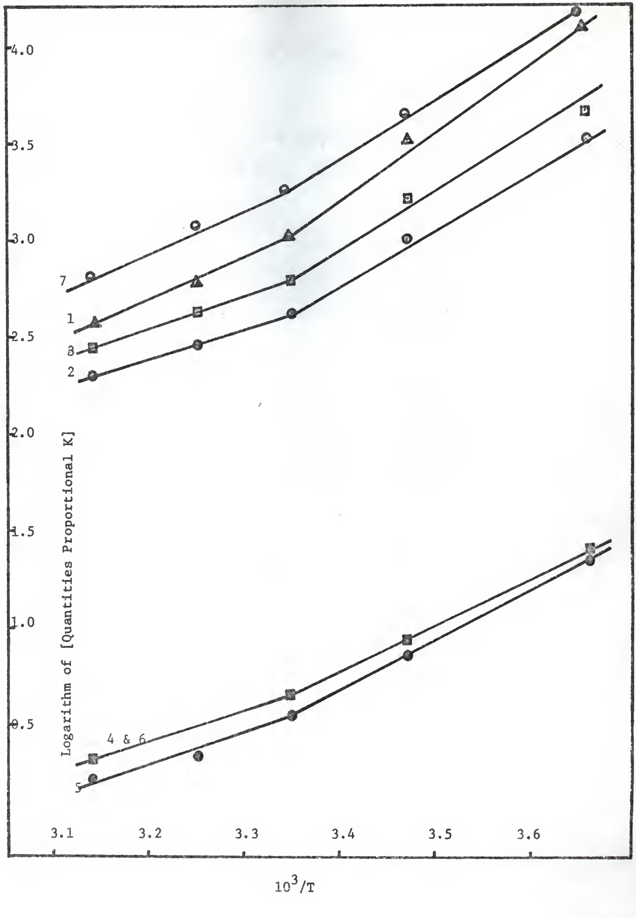

4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
7
1
3
2
4 & 6
5
Logarithm of [Quantities Proportional K]
3.1
3.2
3.3
3.4
3.5
3.6
10^3/T

Figure 13 Plots to Obtain ΔH from Band I for 2-<u>tert</u>-butylphenol

1) Intercept from Ln A_f vs. Ln A_o plots (Table XIII).

2) Logarithm of A_f/A_o^2 average value for all concentrations.

3) Logarithm of A_f/A_o^2 best average value.

4) Logarithm of A_f/A_o^2 average values for all concentrations corrected.

   for changes in the absorption coefficients using temperature dependent a_m' values and a_f values calculated not using Masschelein X values.

5) Logarithm of A_f/A_o^2 average value for all concentrations corrected for changes in the absorption coefficients using temperature independent a_{mI} values and a_f values calculated not using Masschelein X values.

6) Logarithm of A_f/A_o^2 average value for all concentrations corrected for changes in the absorption coefficients using temperature dependent a_m values and a_f values calculated using Masschelein X values.

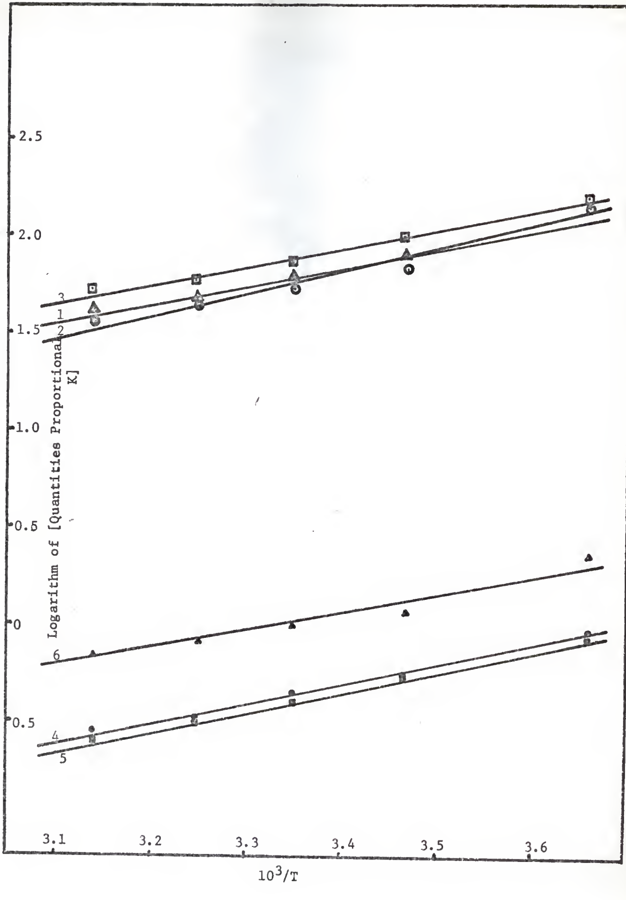

2.5
2.0
1.5
1.0
0.5
0
0.5
3
1
2
6
4
5
Logarithm of [Quantities Proportional K]
3.1
3.2
3.3
3.4
3.5
3.6
$10^3/T$

Figure 14. Plots to Obtain ΔH from Band II for 2-tert-butylphenol

1) Intercept from Ln A_f vs. Ln A_o plots (Table XIII).

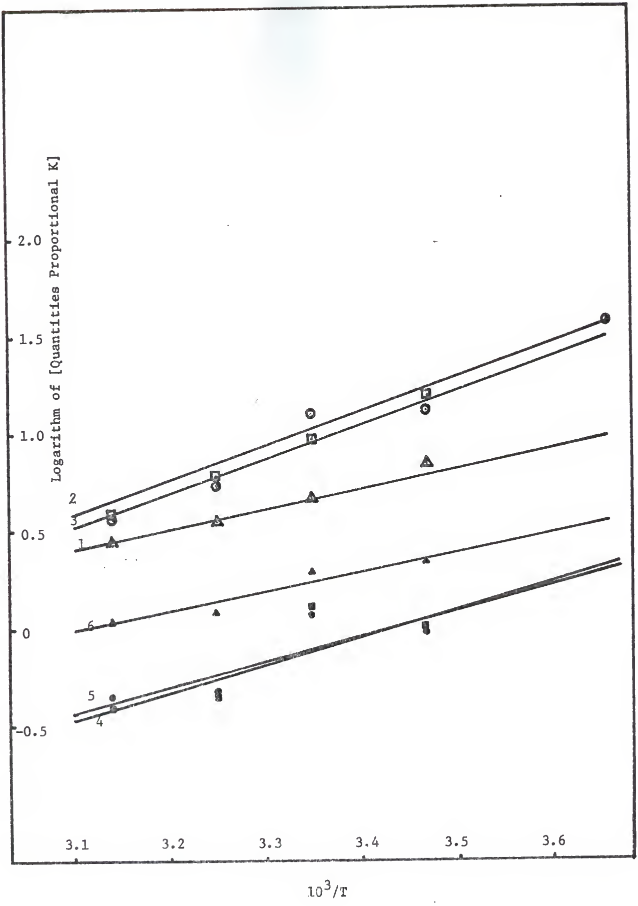
2) Logarithm of A_f/A_o^2 average value for all concentrations.

3) Logarithm of A_f/A_o^2 best average value.

4) Logarithm of A_f/A_o^2 average values for all concentrations corrected for changes in the absorption coefficients using temperature dependent a_m values and a_f values calculated not using Masschelein $\bar{X}$ values

5) Logarithm of A_f/A_o^2 average value for all concentrations corrected for changes in the absorption coefficients using temperature independent a_{mI} values and a_f values calculated not using Masschelein X values.

6) Logarithm of A_f/A_o^2 average value for all concentrations corrected for changes in the absorption coefficients using temperature dependent a_m values and a_f values calculated using Masschelein X values.


Logarithm of [Quantities Proportional K]
2.0
1.5
1.0
0.5
0
-0.5
3.1
3.2
3.3
3.4
3.5
3.6
1
2
3
4
5
6
$10^3/T$

as well as using a_m with Masschelein X values. The enthalpies determined from the slopes of these plots are shown in Table XVIII. Table XIX has the enthalpy determined from the logarithm of A_f/A_o^3 compared to some of the values from Table XVIII for 2-isopropylphenol. The value of $[\text{Ln } (A_f/A_o^2) + \text{Ln } (a_m^2/a_f)]$ where a_m was temperature dependent was selected as the best representation of Ln K (Appendix A) and from this equilibrium constant the thermodynamic functions ΔG, ΔH, ΔS for these processes were calculated and the results are in Tables XX and XXI.

The absolute values of the enthalpy of formation for all of these systems seem to be consistently smaller than the usual enthalpy of hydrogen bond formation which is considered to be on the order of -5 kcal/mole. K.B. Whetsel (11) has reported a value of -5.03 kcal/mole for dimer formation of phenol and it is seen that the enthalpies determined in this study are in general smaller. It can be seen from Table XX that the higher the steric hinderance to hydrogen bond formation the less negative the enthalpy of formation. This is consistent with the interpretation that the more sterically hindered an alcohol is to hydrogen bond formation the longer (or weaker) the bond or the less stable the complex will be.

The elbow in the Ln K vs.1/T plots for the 2-isopropylphenol occurs whether the intercept, Ln A_f/A_o^2, Ln A_f/A_o^3 or the corrected $[\text{Ln } (A_f/A_o^2) + \text{Ln } (a_m^2/a_f)]$ is plotted vs. 1/T. This observation might be explained by the stoichiometry change observed in the Ln A_f vs.Ln A_o plots. The higher composite $-\Delta H$ occurs at the lower temperature where the calculation shows a higher value of the number of molecules in the complex. This elbow also appears in the NMR investigations (5) so it is probably not caused by inherent errors in the infrared analysis. It now appears

Table XVIII: $-\Delta H$ Values (kcal/mole) from the Linear Least Squares Slopes of the Quantities Proportional to Ln K *vs.* 1/T

T(°C) Range	B^+	$Ln(A_f/A_o^2)$ all values x	$[Ln(A_f/A_o^2) + Ln(a_m^2/a_f)]$ where a_m was independent	temperature dependent	dependent #	$Ln(A_f/A_o^2)$ best values *
2,6-di*iso*propylphenol						
0-45	2.3 ± 1.2	1.5 ± 0.4	2.1 ± 0.4	1.4 ± 0.6	0.90 ± 0.5	1.3 ± 0.3
0-35		1.7 ± 0.6	2.2 ± 0.8	1.8 ± 0.4		
0,25,45	1.9 ± 3.5					
2-methyl-6-*tert*-butylphenol						
0-35		0.58 ± 0.4	-0.29 ± 0.15	0.45 ± 2.55		
0-45	-0.26 ± 1.80				0.71 ± 0.9	
2-*iso*propylphenol		band I				
0-25		4.1 ± 0.5	5.2 ± 1.0	4.6 ± 0.8	4.6 ± 0.8	3.8 ± 1.0
25-45		1.4 ± 1.8	2.6 ± 2.8	2.9 ± 0.2	2.9 ± 0.2	2.6 ± 0.5
0-45	4.6 ± 0.9					3.3 ± 0.4
0-35	5.1 ± 0.8					
0,15,35	5.0 ± 1.0					
		band II				
0-25		5.8 ± 2.0	5.4 ± 1.1	4.7 ± 0.3	4.7 ± 0.3	5.6 ± 4.4
25-45		3.1 ± 0.4	3.1 ± 3.9	3.5 ± 0.9	3.5 ± 0.9	3.2 ± 1.1
0-45	6.2 ± 1.1					4.8 ± 0.9
0-35	6.7 ± 1.3					
0,15,35	6.0 ± 1.2					

Table XVIII continued:

T(°C) Range	B^{+}	$Ln(A_f/A_o^2)$ all values X	$[Ln(A_f/A_o^2) + Ln(a_m^2/a_f)]$ where a_m was independent	temperature dependent	dependent#	$Ln(A_f/A_o^2)$ best values *
2-tert-butylphenol		band I				
0-45		2.3 ± 0.8	2.1 ± 0.4	2.4 ± 0.5	1.8 ± 0.5	1.8 ± 0.4
0-35		2.6 ± 1.2	2.3 ± 0.4	2.6 ± 0.8		
0-25		3.1 ± 3.3	2.4 ± 1.3	2.8 ± 3.0		
15-45	1.9 ± 0.5					
		band II				
0-45		3.8 ± 1.0				
15-45	2.41 ± 0.05		2.5 ± 3.6	3.0 ± 3.9	2.0 ± 1.1	3.7 ± 0.3
0,35,45		3.9 ± 0.9				

\# a_f calculated using Masschelein x values
\+ intercepts from Table XIII
x average shown in Tables IX-XII of all values from Tables V-VIII
* averages taken over the following concentrations
2,6-diisopropylphenol - 0.8430, 1.2758, and 1.4188 M
2-methyl-6-tert-butylphenol same as all values
2-isopropylphenol - 0.2416, 0.2990, and 0.3820 M
2-tert-butylphenol - 0.0719, 0.2190, and 0.3613 M

Table XIX: $-\Delta H$ Values (kcal/mole) from the Linear Least Squares Slopes of Quantities Proportional To LnK vs. 1/T for 2-isopropylphenol

T(°C) Range	$Ln(A_f/A_o^2)$ all values #	$[Ln(A_f/A_o^2 + Ln(a_m^2/a_f)]$ a_m temperature dependent+	$Ln(A_f/A_o^3)$ all values x	$Ln(A_f/A_o^2)$ best values*
	band I			
0-25	4.1 ± 0.5	4.6 ± 0.8	4.3 ± 0.2	3.8 ± 1.0
25-45	1.4 ± 1.8	2.9 ± 0.2	3.1 ± 3.3	2.6 ± 0.5
0-45				3.3 ± 0.4
	band II			
0-25	5.8 ± 2.0	4.7 ± 0.3	6.0 ± 1.9	5.6 ± 4.4
25-45	3.1 ± 0.4	3.5 ± 0.9	4.0 ± 2.2	3.2 ± 1.1
0-45				4.8 ± 0.9

\# from Table XVIII

* for concentrations 0.2416, 0.2990, and 0.3820 M

Probable errors calculated at 90% confidence

\+ Since Masschelein X = 1.0 for 2-isopropylphenol this column is the same as both the 5th and 6th columns in Table XVIII

x Average shown in Tables IX to XII of all values from Table V to VIII.

Table XX: Thermodynamics from Plots of $[Ln(A_f/A_o^2) + Ln(a_m^2/a_f)]$ vs.1/T

T(°C)	K liters/ mole	ΔG° cal/ mole	−ΔH°* kcal/ mole	−ΔS° e.u.	
2,6-di*iso*propylphenol					
0	0.293	665.59		9.03	
15	0.247	799.45		9.03	
25	0.215	908.92	1.8 ± 0.4	9.09	
35	0.203	974.92		9.01	
45	0.208	992.67		9.41	
2-methyl-6-*tert*-butylphenol					
0	0.228	801.74		4.58	
15	0.173	1005.46		5.05	
25	0.211	922.54	0.45 ± 2.55	4.61	
35	0.199	988.38		4.67	
2-*iso*propylphenol	band I				
0	2.49	−495		15.0	
15	1.58	−261	4.6 ± 0.8	15.1	
25	1.23	−122		15.0	9.34
35	1.05	−30	2.9 ± 0.2		9.34
45	0.90	+66			9.34
	band II				
0	2.48	−494		15.4	
15	1.57	−258	4.7 ± 0.3	15.4	
25	1.20	−108		15.4	11.4
35	1.02	−13	3.5 ± 0.9		11.3
45	0.83	+117			11.4
2-*tert*-butylphenol	band I				
0	0.952	−26.58		8.69	
15	0.757	159.09		8.88	
25	0.687	222.05	2.4 ± 0.5	8.80	
35	0.599	313.96		8.81	
45	0.559	367.75		8.70	
	band II				
15	0.997	1.72		10.42	
25	1.11	−62.17	3.0 ± 3.9	9.86	
35	0.708	211.14		10.43	
45	0.668	254.64		10.23	

* Probable errors calculated at 90% confidence level

Table XXI: Thermodynamics from Plots of [Ln (A_f/A_o^2) + Ln (a_m^2/a_f)] vs. 1/T using Masschelein X values to calculate a_f

T(°C)	K	ΔG°	-ΔH*	-ΔS°	
2,6-di<u>iso</u>propylphenol	1/mole	cal/mole	kcal/mole	e.u.	
0	0.468	412.0		4.82	
15	0.420	497.0		4.85	
25	0.388	562.0	0.90 ± 0.5	4.90	
35	0.367	613.0		4.92	
45	0.380	613.0		4.67	
2-methyl-6-<u>tert</u>-butylphenol					
0	0.317	624.0		4.90	
15	0.262	768.0		5.14	
25	0.298	718.0	0.71 ± 0.9	4.80	
35	0.284	760.0		4.77	
45	0.244	894.0		5.05	
2-<u>iso</u>propylphenol	band I				
0	2.49	-495		15.0	
15	1.58	-261	4.6 ± 0.8	15.1	
25	1.23	-122		15.0	9.34
35	1.05	-30	2.9 ± 0.2		9.34
45	0.90	+66			9.34
	band II				
0	2.48	-494		15.4	
15	1.57	-258	4.7 ± 0.3	15.4	
25	1.20	-108		15.4	11.4
35	1.02	-13	3.5 ± 0.9		11.3
45	0.83	+117			11.4
2-<u>tert</u>-butylphenol	band I				
0	1.40	-182.0		7.29	
15	1.06	- 33.0		6.38	
25	0.995	+2.9	1.8 ± 0.5	6.03	
35	0.915	+54.4		5.68	
45	0.865	+91.6		5.37	
	band II				
15	1.40	-192.0		6.29	
25	1.33	-168.8		6.14	
35	1.09	-52.6	2.0 ± 1.1	6.30	
45	1.04	-24.6		6.22	

* Probable error calculated at 90% confidence level

resonable to suspect a continous change in the average stoichiometry with changes in temperature or concentration for 2-isopropylphenol in carbon tetrachloride.

Peak Intensity Ratios

The overtone spectra of 2-*tert*-butylphenol and 2-methyl-6-*tert*-butylphenol have an absorbance peak at a slightly lower wavelength than the large absorbance. Table XXII shows that the ratio of this small peak to the large peak is constant within experimental error over both concentration and temperature. The absorbance of the higher frequency is about 7.5 percent of the lower frequency absorbance for 2-*tert*-butylphenol and about 12.0 percent for 2-methyl-6-*tert*-butylphenol. This observation is consistent with that of Sakano *et*. *al*. (12) who observed that for the fundamental absorbance spectra of 2-*tert*-butylphenol and 2-methyl-6-*tert*-butylphenol the absorbances near 3645 cm^{-1} were 7.0 percent and 20 percent, respectively, of those near 3610 cm^{-1}. They state "Apparently an *ortho*-tert-butyl group forces the OH group into a conformation having a higher OH stretching frequency than that customary for an alkyl phenol." It therefore appears that through these temperature ranges the monomers of these two phenols exists as two definite species as evidenced by the fundamental and overtone spectra with the band intensity ratio independent of concentration and temperature.

Table XXII Ratio of Small Band Absorbance to the Large Band Absorbance Per Cm Cell Length

T(°C)	C(M)	Small	Large	Small/ Large
2-*tert*-butylphenol				
0	0.1479	0.035	0.458	0.076
15	0.1462	0.025	0.445	0.056
25	0.1438	0.030	0.443	0.068
35	0.1421	0.035	0.440	0.079
0	0.2253	0.052	0.656	0.079
15	0.2228	0.048	0.646	0.074
25	0.2190	0.048	0.640	0.075
35	0.2165	0.054	0.641	0.084
45	0.2139	0.055	0.637	0.086
0	0.3719	0.075	0.925	0.081
15	0.3677	0.074	0.936	0.079
25	0.3613	0.075	0.942	0.079
35	0.3570	0.080	0.951	0.084
45	0.3528	0.086	0.948	0.091
2-methyl-6-*tert*-butylphenol				
0	0.9895	0.25	2.27	0.110
15	0.9781	0.27	2.18	0.123
25	0.9667	0.26	2.18	0.119
35	0.9553	0.27	2.14	0.126
45	0.9438	0.28	2.10	0.133
0	1.3228	0.28	2.82	0.132
15	1.2995	0.30	2.77	0.108
25	1.2841	0.35	2.72	0.128
35	1.2687	0.37	2.68	0.138
45	1.2533	0.40	2.65	0.151
0	1.5017	0.30	3.11	0.097
15	1.4749	0.37	3.10	0.119
25	1.4570	0.40	3.03	0.132
35	1.4391	0.40	2.95	0.135
45	1.4213	0.45	2.95	0.152
0	1.5149	0.47	3.16	0.149
15	1.4954	0.42	3.09	0.136
25	1.4771	0.40	3.06	0.130
35	1.4588	0.37	3.05	0.121
45	1.4406	0.37	3.03	0.122

CONCLUSIONS

The most important results of this study may be summarized as follows:

1) All of the phenols investigated associate with monomer dimer as the most probable process except 2-*iso*propylphenol where trimers along with dimers in equilibrium with monomer appear to best represent the association process over the concentration ranges investigated.
2) The absorption coefficient of both the fundamental and the overtone bands (a_f and a_m respectively) was found to be temperature dependent.
3) The free OH overtone bands showed a contribution from the free OH end groups of the complex as determined by the Masschelein technique for all systems except 2-*iso*propylphenol.
4) The $|\Delta H|$ determined from the Logarithm of [Quantities Proportional to K] *vs.* 1/T plots for these sterically hindered phenols were all anomalously low compared to the usual hydrogen bond energies of 4-5 kcal/mole.

Appendix A

Some Relations between Thermodynamic Functions and Spectroscopically Measured Quantities

This appendix shows how the logarithm of the equilibrium constant can be obtained from the logarithm of the A_f/A_o^2 ratios and how the intercepts from Ln A_f vs. Ln A_o are proportional to the equilibrium constant. The correction for the temperature dependent absorption coefficients made on A_f/A_o^2 to obtain a correct expression for the equilibrium constant was accomplished as follows. The concentration of complex and monomer is given by:

$$C_{complex} = A_f/a_f$$

$$C_{monomer} = A_o/a_m$$

where A_f and a_f are the absorbances per cm path length and the absorption coefficient for the complex absorbance of the 3500 cm^{-1} band, respectively, and A_o and a_m are the absorbance per cm path length of the 7100 cm^{-1} band, and the absorption coefficient for the monomer respectively.

The equilibrium constant expression takes the form:

$$K = (A_f/a_f)/(A_o/a_m)^{\underline{n}} = (C_{complex})/(C_{monomer})^{\underline{n}}$$

Taking the natural logarithm of this expression one obtains

$$\text{Ln } K = \text{Ln}[(A_f/a_f)/(A_o/a_m)^{\underline{n}}] = \text{Ln } A_f - \text{Ln } a_f + \underline{n}\text{Ln } a_m - \underline{n}\text{Ln } A_o.$$

Since the values of Ln $(A_f/A_o^{\underline{n}})$ were available the correction for temperature dependent absorption coefficients was made on this function in the following manner: Ln $K = \text{Ln}[(A_f/A_o^{\underline{n}}) + \text{Ln } (a_m^{\underline{n}}/a_f)]$ where $\underline{n}$ takes on the value of two for dimers. This Ln K was plotted against 1/T to determine the ΔH of complex formation.

The affect of temperature dependent absorption coefficients on the intercepts from the Ln A_f vs. Ln A_o may be shown in the following manner:

Assume 1) A_f due only to one complex species
2) A_o due only to monomer

If A_f/A_o^n is a constant, Ln A_f vs. Ln A_o should be a straight line with a slope equal to the number of molecules in the complex. The intercept, (B), is proportional to the logarithm of the equilibrium constant $K_n = C_n/C_m^n = (A_f/a_f)/(A_o/a_m)^n$ since Ln K = Ln A_f − Ln a_f − nLn A_o + nLn a_m or arranging Ln A_f = nLn A_o + Ln (K a_f/a_m^n) thus B = Ln (K a_f/a_m^n). If (a_f/a_m^n) is temperature independent a plot of B vs. 1/T will give a slope $-\Delta H/R$. Since $\Delta G = \Delta H - T\Delta S$ at constant temperature, assuming ΔH and ΔS are not functions of temperature, one obtains

$$\Delta G = -RT \text{ Ln } K = \Delta H - T\Delta S$$

and

$$\text{Ln } K = -(\Delta H/R)(1/T) - \Delta S/R.$$

The plot of (B) vs. 1/T takes the following form

$$[\text{Ln } K + \text{Ln } (a_f/a_m^n)] = -\Delta H/R(1/T) - \Delta S/R + \text{Ln } (a_f/a_m^n).$$

Therefore, it appears that the absorption coefficient expression affects the intercept and not the slope if (B) is plotted against 1/T. This (B) was plotted against 1/T to determine ΔH of complex formation.

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LITERATURE CITED

1. G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond", W. H. Freeman, San Franciso, 1960., p. 66.

2. A. N. Fletcher and C. Heller, J. Phys. Chem., 71, 3742(1967).

3. R. M. Hammaker, R. M. Clegg, L. K. Patterson, P. E. Rider and S. L. Rock, J. Phys. Chem. 72, 1837(1968).

4. A. N. Fletcher and C. Heller, J. Phys. Chem., 72, 1839(1968).

5. L. K. Patterson, "Hydrogen Bonding: Some Infrared and NMR Studies of Hindered Alcohols", Doctoral Dissertation, Kansas State University, 1967; L. K. Patterson and R. M. Hammaker, Unpublished Studies.

6. C. A. Swenson, J. Phys. Chem., 72, 3108 (1967).

7. R. M. Hammaker, Private Communication.

8. A. Ens. and F. E. Murray, Can. J. Chem., 35, 170(1957).

9. W. Masschelein, Spectrochim Acta, 18, 1557(1962).

10. P. E. Rider, Private Communication.

11. K. B. Whetsel and J. H. Lady, To be published in the Advances in Chemistry Series.

12. T. K. Sakano, S. L. Rock, and R. M. Hammaker, Spectrochim Acta, 26A, 0000(1969).

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A SPECTROSCOPIC STUDY OF THE SELF ASSOCIATION OF SOME ALKYL PHENOLS

by

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The intermolecular self association of 2-isopropylphenol, 2-tert-butylphenol, 2,6-diisopropylphenol and 2-methyl-6-tert-butylphenol was investigated using infrared and near infrared spectroscopy. The infrared spectrum of each compound at several concentrations and at five temperatures was taken for the fundamental OH stretching region and the intensity of the band or bands appearing at frequencies lower than the free OH vibration was employed as a measure of the complex concentration. The near infrared spectrum of each compound at several concentrations and five temperatures was also taken in the region of the first overtone of the OH vibration and the intensity of this band was employed as a measure of the monomer concentration. The monomer absorption coefficient was determined for each compound from the intensity of this band at five temperatures in an attempt to determine if it was temperature dependent.

An attempt to determine the stoichiometry of the complex formation was carried out at each temperature. This calculation divided the intensity of the 3500 cm^{-1} band by the intensity of the 7100 cm^{-1} band raised to the $\underline{n}^{th}$ power where $\underline{n}$ ranges from one to three for each concentration at constant temperature. The value of $\underline{n}$ giving the most constant value of this ratio is selected as the number of molecules in the complex. If this ratio is constant for some $\underline{n}$ then a plot of Ln A_f vs. Ln A_o should be linear with a slope of $\underline{n}$. These plots were prepared to determine if the $\underline{n}$ was the same as that determined from the A_f/A_o calculation for each compound at each temperature. This enabled the determination of temperature dependence or independence of the number of molecules forming the complex.

Linear least squares plots of Ln $(c-c_1)$ vs. Ln c_1 were prepared where c is the total concentration and c_1 is the monomer concentration with no correction for the complex OH end group contribution to the monomer absorbance. It was found that the slopes were in general larger than the slope for the Ln A_f vs. Ln A_o plots. The technique of Masschelein (Spectrochim Acta 18, 1557 (1962)) was employed to determine the extent of the complex OH end group contribution to the free OH band.

The quantity Ln (A_f/A_o^2) was corrected for absorption coefficient change with temperature and this corrected quantity was employed as the best Ln K from which the thermodynamic functions ΔG, ΔH, ΔS were obtained.